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Part III

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RESEARCH ON SYNTHESIS PROCEDURES FOR INTERMEDIATES REQUIRED FOR HIGH TEMPERATURE STABLE POLYMERS

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August 1972

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Air Force Materials Laboratory
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RESEARCH ON SYNTHESIS PROCEDURES FOR INTERMEDIATES
REQUIRED FOR HIGH TEMPERATURE STABLE POLYMERS

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-71-C-1128, "Research on Synthesis Procedures for Intermediates Required for High Temperature Stable Polymers." The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. George Moore (LNP), as Project Scientist.

This technical report covers the work conducted from January 1971 to May 1972. The manuscript was released by the authors in June 1972 for publication as a technical report.

The work was carried out by Mr. G. L. Whittier, Mr. J. F. Engel, Dr. C. W. Kruse and Dr. C. C. Chappelow, Jr., who served as Principal Investigator.

This technical report has been reviewed and is approved.



R. L. VAN DEUSEN
Chief, Polymer Branch
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ABSTRACT

Work is reported on the synthesis and/or characterization of 30 different compounds for use in studies related to the preparation of high-temperature stable polymers. As a result of this effort, 28 synthesized and/or characterized compounds were submitted as 42 individual samples. The number and type of compounds submitted are identified as follows:

- 2 - Perfluoro-n-alkyl iodides
- 2 - Divinyl substituted aromatics
- 2 - Organo-diiodides
- 5 - Acenaphthene derivatives
- 3 - Diether linked dicarboxylic acids
- 3 - Aromatic disulfonamides
- 2 - Perfluoroalkylene bisphenols
- 2 - Perfluorophenyl thiols
- 1 - Ladder polymer
- 3 - Substituted polyphenyl ethers
- 3 - Substituted phenyl halides

The 42 samples of the submitted compounds ranged in size from 2.0 to 650.4 g and, in nearly all cases, the purity was at least 99%. Mass spectrometry, infrared spectroscopy, gas liquid chromatography, nuclear magnetic resonance spectroscopy, thin-layer chromatography, differential thermal analysis, viscosimetry, and elemental analysis were employed to establish structure and determine purity.

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SECTION I

INTRODUCTION

The purpose of this research program was to synthesize and characterize various classes of compounds for use in the preparation of high temperature stable polymers. The synthetic schemes utilized in this work were based on either improved established preparative procedures or newly devised, unique synthetic methods.

Work was conducted on the synthesis and/or characterization of 30 different compounds. As a result of this effort, a total of 42 individual samples of 28 different compounds were submitted to the Polymer Branch, Air Force Materials Laboratory. In nearly all cases, the purity of the samples submitted was at least 99% pure. The compounds and the number of samples shipped are listed as follows.

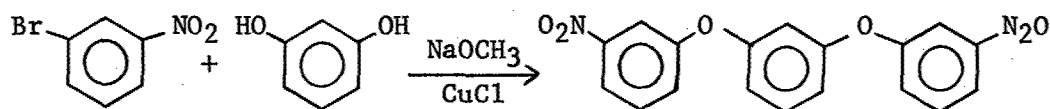
	<u>Samples</u>
Perfluoro- <u>n</u> -octyl iodide	4
1,3-Bis(3-nitrophenoxy)benzene	1
1,3-Bis(3-aminophenoxy)benzene	1
1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene	3
1'-Methyl-2,3-cyclopentenoacenaphthene	1
Pyracen-1,2-dione	1
2,3,5,6-Tetrafluorothiophenol	1
β -(3-Acenaphthoyl)propionic acid	1
3,6-Dioxaoctanedioic acid	1
4,8-Dioxaundecanedioic acid	1
1,8-Divinyl naphthalene	2
Bis-5,5'-acenaphthenyl(1,3-phenyl)ketone	1
5-Methyl-4,7-dioxadecanedioic acid	1
4,5-Dinitro-N,N'- <u>o</u> -phenylenebis(<u>p</u> -toluenesulfonamide)	2
2,3,5,6-Tetrafluorobenzene-1,4-dithiol	1
Perfluoro- <u>n</u> -decyl iodide	3
1,3-Diiodohexafluoropropane	2
4-Iodophenyl acetate	2
1,3-Bis(3-nitro-4-hydroxyphenyl)hexafluoropropane	1
4,8-Dibromo-1,5-bis(<u>p</u> -toluenesulfonamido)naphthalene	1
1,3-Bis(4-hydroxyphenyl)hexafluoropropane	1
2,2'-Diiodobenzidine	2
<u>o</u> -Divinylbenzene	2
BBL Polymer	2
3,3'-Dinitro-N,N'-di- <u>p</u> -toluenesulfonyl benzidine	1
1,2-Dinitro-4-fluorobenzene	1
<u>p</u> -Iodo- <u>o</u> -nitroaniline	1
1,3-Bis(3,4-dinitrophenoxy)benzene	1

SECTION II

PREPARATION AND CHARACTERIZATION OF COMPOUNDS

1. 1,3-Bis(3-nitrophenoxy)benzene

This compound was prepared in a 25% yield via the following reaction sequence (Ref. 1).



a. Synthesis: Sodium methoxide (0.492 mole) was prepared by adding 11.3 g (0.492 g.-atom) of sodium spheres to 100 ml of anhydrous methanol under an argon atmosphere. After complete reaction, excess methanol was distilled with last traces removed by sweeping with argon. To the solid sodium methoxide was added 500 ml of benzene which had been dried by distillation of approximately 10% of its volume. The mixture was heated to reflux, and 50 ml of solvent was distilled to remove any traces of methanol. Resorcinol (27.6 g, 0.250 mole) was added, and the benzene removed by distillation. The salt was cooled, and 500 ml of pyridine (dried by distillation over calcium hydride) was added. To the slurry was then added a mixture of 7.6 g of cuprous chloride in 200 g (1.0 mole) of *m*-bromonitrobenzene. The reaction mixture was heated under reflux overnight, then allowed to stand at room temperature for 2 days.

The mixture was poured into 1,200 ml of water, acidified to pH 2 with concentrated hydrochloric acid, and extracted with benzene. The benzene solution was washed twice with 10% aq. NaOH and with water. After drying with Na_2SO_4 , the benzene was evaporated in vacuo to afford a yellow oil. An attempt to distill unreacted *m*-bromonitrobenzene (b.p. $153^\circ\text{C}/60$ torr) was abandoned when the material in the distillation flask began to discolor.

The crude product was then dissolved in hot ethanol. On cooling, a yellow oil separated out of solution. The oil crystallized on further cooling and stirring. The solid was filtered, and a second crop of crystals precipitated from the filtrate. The infrared spectrum and m.p. identified the second crop as *m*-nitrobromobenzene.

The first crop was recrystallized repeatedly from ethanol to afford 22.5 g (25%) of 1,3-bis(3-nitrophenoxy)benzene, m.p. $104.5\text{--}106^\circ$ (reported m.p. $104\text{--}105^\circ$) (Ref. 1).

* All temperatures are reported in $^\circ\text{C}$.

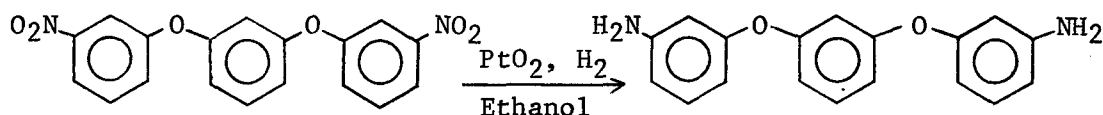
b. Physical Properties: 1,3-Bis(3-nitrophenoxy)benzene was a yellow solid, m.p. 104.5-106°. Its infrared spectrum is reported in Figure 1.*

c. Purity: An elemental analysis of the compound indicated the purity to be 99+%.

Anal. Calcd. for $C_{18}H_{12}N_2O_6$: C, 61.36; H, 3.43; N, 7.95, Found: C, 61.05, H, 3.19; N, 8.12.

2. 1,3-Bis(3-aminophenoxy)benzene

This material was synthesized by catalytic hydrogenation of 1,3-di(3-nitrophenoxy)benzene in 75% yield (Ref. 1).



a. Synthesis: Adams catalyst (0.2 g, PtO_2) was dispersed in 300 ml of absolute ethanol and hydrogenated at 50 psig for 10 min. in a Parr hydrogenation apparatus. Then 12.5 g (0.035 mole) of 1,3-di(3-nitrophenoxy)benzene (I) was added, and the reactor pressurized to 55 psig. The theoretical amount of hydrogen (16 psig) was taken up in 15 min. After shaking an additional 10 min., the reaction mixture was filtered and the ethanol evaporated in vacuo to afford a yellow oil. Trituration of the oil with a mixture of petroleum ether (b.p. 60-90°) and a small amount of ethanol gave yellow crystals which were recrystallized from a benzene-petroleum ether mixture to afford 7.8 g (75%) of 1,3-bis(3-aminophenoxy)benzene, m.p. 106.5-108° (reported m.p. 107-108°) (Ref. 1).

b. Physical Properties: 1,3-Bis(3-aminophenoxy)benzene was a yellow crystalline solid, mp 106.5-108°. The infrared spectrum appears as Figure 2.

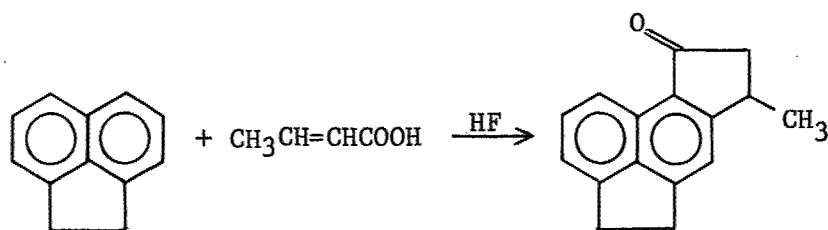
c. Purity: The purity was assayed at 99+% based on elemental analysis.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.24. Found: C, 74.12; H, 5.49; N, 9.45.

3. 1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene

This compound was prepared by the hydrogen fluoride catalyzed condensation of acenaphthene and crotonic acid in yields ranging from 23-39% (Ref. 2).

* All figures are found at the end of the report, pp. 51-116.



a. Synthesis: A mixture of 54.3 g (0.35 mole) of freshly sublimed acenaphthene and 30.4 g (0.353 mole) of crotonic acid in 340 g of anhydrous hydrogen fluoride was allowed to stand at room temperature for 24 hr. Occasional manual stirring was employed at the start.

The mixture was then heated on a steam bath to evaporate the remaining hydrogen fluoride. The residue was dissolved in benzene, and the solution was washed with aqueous sodium bicarbonate and water. Evaporation of the benzene left a brown oil which was distilled through a short path system to afford 43.0 g of a brown solid (b.p. 180-210°/0.1 mm). The crude product was recrystallized from a mixture of benzene and petroleum ether (b.p. 60-90°) and finally from a 4:1 mixture of methanol and benzene. Final yield of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene was 30.0 g (39%), m.p. 165-165.5 (reported m.p. 167-167.5°) (Ref. 2).

A reaction on a 0.70 mole scale gave no product when the same procedure was used. However, a second large-scale reaction which was stirred magnetically overnight afforded 58.3 g of crude 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene. This sample was combined with an additional 60.0 g of crude product obtained from two small scale runs, and recrystallized twice from benzene-petroleum ether to afford 93.0 g (29% average yield) of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene, m.p. 165-165.5°.

An additional 218.0 g of crude product was obtained from five reactions carried out by the following modified procedure. A mixture of 108.6 g (0.71 mole) of recrystallized acenaphthene, 60.8 g (0.71 mole) of crotonic acid and 340 g of anhydrous hydrogen fluoride was stirred overnight in a covered beaker. Excess hydrogen fluoride was then removed by sweeping with nitrogen. The solid residue was dissolved in 1,500 ml of benzene and the solution washed with aqueous sodium carbonate. The organic layer was then washed three times with water and dried. The benzene solution was concentrated to approximately 300 ml, diluted with an equal volume of petroleum ether (b.p. 60-90°) and chilled. The precipitated material was filtered, washed with petroleum ether and air dried to give 43.5 g of crude product.

The combined crude samples from the five reactions were then distilled through a Claisen head [b.p. 180-200° (0.1 mm)], and recrystallized from

benzene and petroleum ether (b.p. 60-90°) to afford 180.0 g (23% average yield) of light tan product, m.p. 171-172° (reported m.p. 167-167.5°) (Ref. 2).

An additional two reactions were carried out on a 0.71 mole scale. Because the combined crude products isolated from the benzene extractions were found to be of high purity after several petroleum ether washings, the usual distillation step was avoided. A single recrystallization of the product from benzene-petroleum ether gave 93.0 g (30%) of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene, m.p. 171.5-173°.

b. Physical Properties: 1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene was a light tan solid, m.p., 171-172°. The infrared and NMR spectra are reported as Figures 3 and 4.

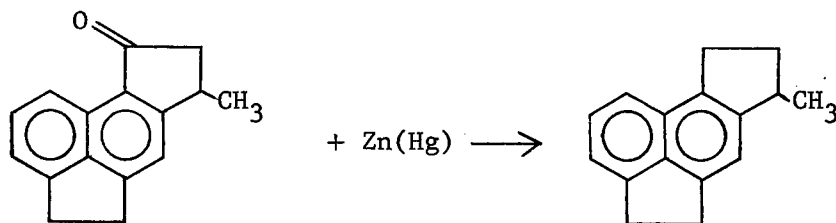
c. Purity: All recrystallized samples were of 99% purity by gas-liquid chromatography (GLC) [2m, 5% SF-96 on Gas Chrom Q, 225°, He carrier: 15 psig, flame ionization detector (FID)]. A typical chromatogram is reported as Figure 5.

An elemental analysis was obtained on one sample.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 87.07; H, 6.35.

4. 1'-Methyl-2,3-cyclopentenoacenaphthene

A 25.0 g sample of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene was converted in a 40% yield to 1'-methyl-2,3-cyclopentenoacenaphthene via reduction with zinc amalgam (Ref. 2).



a. Synthesis: To a mixture of 47 g (0.725 mole) of zinc amalgam (Ref. 3) with 125 ml of concentrated hydrochloric acid, 50 ml of water, 75 ml of toluene, and 3 ml of glacial acetic acid was added 25.0 g (0.11 mole) of 1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene. The mixture was heated under reflux with vigorous stirring for 17 hr. An additional 175 ml of concentrated hydrochloric acid was added and refluxing continued for 7 hr. The organic layer was separated, and the toluene evaporated in vacuo to afford a viscous yellow oil. The crude product was repeatedly recrystallized from aqueous methanol to afford 7.5 g (40%) of colorless cottony needles, m.p. 36-36.5° (reported m.p., 38-38.5°) (Ref. 2).

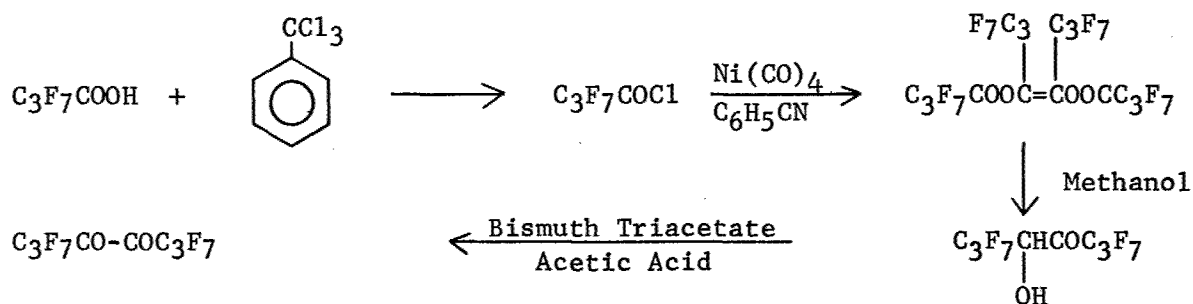
b. Physical Properties: 1'-Methyl-2,3-cyclopentenoacenaphthene had the appearance of colorless needles, m.p., 36-36.5°. The infrared and NMR spectra are reported in Figures 6 and 7.

c. Purity: Purity was assayed at 98% by GLC (2 m, 5% SF-96 on Gas Chrom Q, 190, He carrier: 15 psig, FID).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.85; H, 7.53.

5. Perfluoro-4,5-octanedione

Drysdale and Coffman report the following reaction sequence for the preparation of this compound (Ref. 4).



The synthesis of heptafluorobutyryl chloride proceeded without difficulty in 71% yield. However, the reaction to the next intermediate was unsuccessful on two attempts. The only identifiable material isolated on treatment of the acid chloride with nickel carbonyl in the presence of benzonitrile was a small amount of by-product, 5-hydroxotetradecafluoro-4-oxo-5-octyl perfluorobutyrate.

Synthesis: A mixture of 214.0 g of heptafluorobutyric acid and 391.0 g (2.0 mole) of α,α,α -trichlorotoluene was heated in a three-necked flask equipped with stirrer, thermometer, and a 30-cm Vigreux column topped with a fractional distillation head. At reaction temperatures of 100-210° the acid chloride was distilled and collected over a boiling range of 39-52°. Final yield of heptafluorobutyryl chloride was 162 g (71%). The infrared spectrum of the colorless liquid is reported in Figure 8.

A pilot scale preparation of perfluoro-4-octene-4,5-diol di-(perfluorobutyrate) was attempted on a 0.61 mole scale. Nickel carbonyl (25 g) was added under anhydrous conditions to a mixture of 160 g of heptafluorobutyryl chloride (b.p. 39-52°) and 64.0 g (0.61 mole) of benzonitrile. An additional 15 g of nickel carbonyl was added after stirring the reaction at room

temperature for 72 hr. A third addition of 15 g of nickel carbonyl was made at 120 hr, then stirring was continued for 7 days. The yellow reaction mixture, which contained finely divided solid, was diluted with a solution of 50 ml of ethyl ether and 70 ml of benzene. The ether was distilled to remove unreacted nickel carbonyl. Distillation was continued until addition of an ether-iodine solution to the distillate gave a persistent iodine color.

Filtration of the mixture was very difficult because the fine solid continually clogged the filter surface. The filtration was completed after 1.5 hr by frequent reslurry of the mixture with additional ether. Ether was then evaporated in vacuo from the filtrate. Distillation of the brown residue at 18 mm gave only benzonitrile and an intractable distillation residue.

A second reaction on an 0.51 mole scale with redistilled heptafluorobutyryl chloride (b.p. 40-41°) and benzonitrile also gave no product which could be identified as the desired enediol diester. Distillation gave 3.7 g of material which codistilled with benzonitrile at 70-78° (18 mm). The liquid reaction products separated as a heavier phase in the distillation receiver.

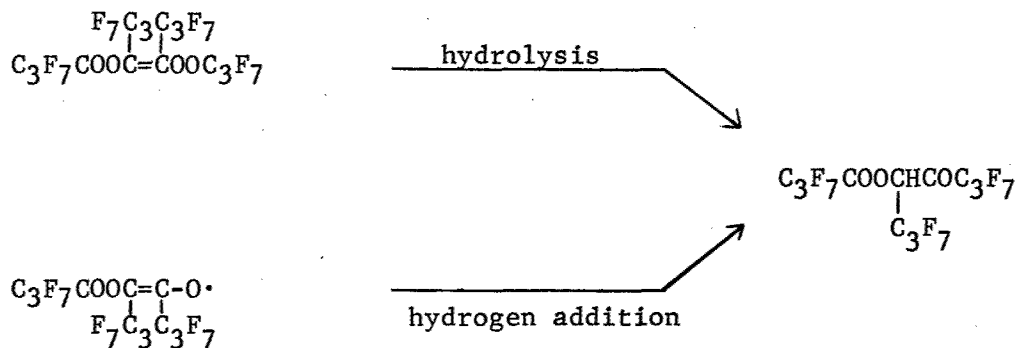
As in the initial attempt to prepare the desired enediol ester, an intractable glassy material was left as distillation residue. The residue accounted for 45% of recovered mass after distillation.

The infrared spectrum of the lower phase portion of the distillate (see Figure 9) shows a strong carbon-fluorine absorption at 1180-1220 cm^{-1} , a hydroxyl type absorption at 3250 cm^{-1} , and several bands in the carbonyl region with the low wavelength band at 5.55 μ (1900 cm^{-1}). Benzonitrile contamination is also indicated by the presence of the 2225 cm^{-1} absorption.

The low boiling point of the isolated material suggests that the distillate was not the desired enediol diester [reported b.p., 89° (18 mm)]. Also the absence of an infrared carbonyl absorption at the reported 5.45 μ region is further evidence the isolated compound was not perfluoro-4-octene-4,5-diol di-(perfluorobutyrate).

Drysdale and Coffman report the identification of an acyloin ester [b.p. 64° (18 mm)] which could be formed on hydrolysis of the enediol diester or by abstraction of a hydrogen atom from benzonitrile by the intermediate $\text{R}_f\text{COOC}=\text{CO}\cdot$ radical.



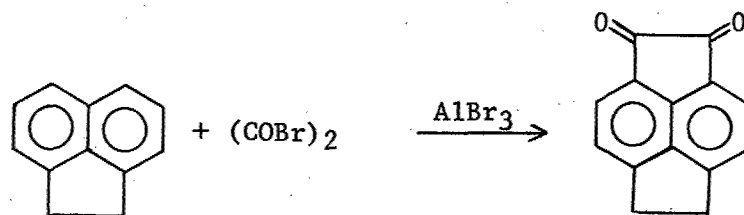


Because of the similarity in boiling point and the hydroxyl infrared absorption which can be attributed to an enol-type structure, the material recovered on distillation was probably the acyloin ester, 5-hydrotetradecafluoro-4-oxo-5-octyl perfluorobutyrate.

In considering possible future attempts in the synthesis of this series, Dr. Drysdale (Ref. 5) was contacted to discuss the reaction procedures, especially problems encountered with filtration of the crude reaction mixture. The following information was obtained: (1) instead of using ethyl ether to aid the filtration, additional benzonitrile should be used; (2) the desired product is insoluble in benzonitrile, therefore, a preliminary separation of the crude product can easily be made before distillation; and (3) it would not be necessary to remove the excess nickel carbonyl via codistillation with ether if all operations were conducted with adequate ventilation.

6. Pyracen-1,2-dione

A total of 20.0 g of this compound was prepared in 15% yield via the aluminum bromide catalyzed condensation of oxalyl bromide and acenaphthene (Refs. 6 and 7).



a. Synthesis: A solution of 100.0 g (0.65 mole) of freshly sublimed acenaphthene in 2 liters of carbon disulfide was cooled to -15°C . (Cooling bath consisted of 1:2.5 methanol:water solution with Dry Ice.) Oxalyl bromide

(219 g, 1.015 mole) was then added. The solution was cooled to -20° and 325.0 g (1.218 mole) of aluminum bromide was added over 2 hr. A black precipitate formed immediately on addition of the aluminum bromide.

The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. After refluxing for 1 hr on a hot water bath, the reaction mixture was cooled and the carbon disulfide was decanted from the black residue. The residue was treated with 2 liters of cold 6 N hydrochloric acid and was stirred until the evolution of hydrogen bromide ceased. The mixture was filtered and the filter cake was washed with water.

The brown solid was slurried with 3 liters of 10% sodium bisulfite for 2 hr at 80° and gravity filtered while hot. The filtrate was heated to 80° and treated with concentrated hydrochloric acid until the evolution of sulfur dioxide ceased. A fluffy yellow precipitate formed. The mixture was stirred an additional 30 min at 80° , then cooled and filtered.

The sodium bisulfite extraction was then repeated five times on the brown reaction product to give a total of 33.0 g of yellow solid. After recrystallization from dimethylformamide, 20.0 g (15%) of orange crystals were obtained. The solid had a melting point with decomposition of $305.5-307^{\circ}$ [reported m.p., $306-307^{\circ}$, (Ref. 6), $294-298^{\circ}$ dec. (Ref. 7)].

b. Physical Properties: Pyracen-1,2-dione was an orange crystalline solid, m.p. $305.5-307^{\circ}$ dec. The infrared and NMR spectra are reported in Figures 10 and 11.

c. Purity: Because the carbon values of triplicate elemental analyses of this compound were found to exceed acceptable limits, additional analytical work was conducted. The experimental results and known literature values (Refs. 6 and 7) are summarized as follows:

Elemental analysis: Two sources (Galbraith Labs., Inc., and the MRI unit) gave carbon values which were low by 4-5%. Hydrogen values, however, were acceptable in both cases.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.87. Found: C, 76.50; H, 3.57 (Galbraith); C, 75.98; H, 3.62 (MRI); C, 77.55; H, 3.33 (MRI).

Infrared spectral data: The infrared spectrum for the sample shows two carbonyl peaks at 1655 cm^{-1} and 1720 cm^{-1} with weak C-H absorptions at 2890 cm^{-1} and 3020 cm^{-1} . A calibration absorption of 1601.4 cm^{-1} for polystyrene occurs at 1600.0 cm^{-1} in the spectrum. Corresponding literature values are 1660, 1735, 2925, and 3050 cm^{-1} (Ref. 6).

NMR spectral data: The reported chemical shift values for pyracen-1,2-dione are 8.12 and 7.72 ppm for the four aromatic protons and 3.76 ppm for the four methylene protons (Ref. 6). The NMR spectrum was obtained on a Varian A-60 spectrometer as a solution in trifluoroacetic acid. Chemical shift values of 8.11 and 7.70 ppm were obtained for the aromatic region (see Figure 6 for actual assignment) and 3.71 ppm for the methylene signal. Integration of the spectrum gave a ratio of 1:1 for the aromatic to methylene proton signals.

UV spectral data: UV spectra were determined as ethanol solutions and were measured with a Beckman DK-1 and a Beckman DK-2. Results and literature values are tabulated below as $m\mu$ (ϵ).

<u>Beckman DK-1</u>	<u>Beckman DK-2</u>	<u>Literature (Ref. 6)</u>
--	--	213 (4,300)
235 (59,716)	235 (64,272)	238 (52,500)
246 (sh; 21,204)	246 (sh; 22,048)	246 (18,200)
--	--	318 (sh; 4,950)
322 (6,710)	324 (8,819)	332 (6,400)
--	--	354 (6,700)
--	--	364 (sh; 5,600)

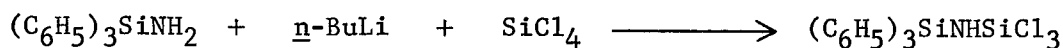
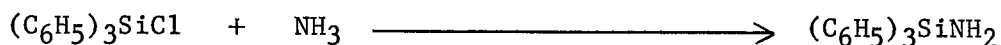
The reported absorption at 213 $m\mu$ could not be determined because of solvent cutoff in the DK-1, and the DK-2 range does not extend to that region. As noted, the 246 $m\mu$ absorption occurred as a shoulder and this may explain the apparent discrepancy between calculated and literature values for the corresponding extinction coefficient. No real evidence was seen of the reported absorptions at 318, 354, and 364 $m\mu$ in our spectra.

Mass spectral data: The mass spectrum gave data which compare well with reported values (Ref. 6). A molecular ion occurred at m/e 208 and abundant peaks were measured at 180 (base peak, M^+-CO), 152 (M^+-2CO), 151 ($M^+-2CO-H$) and 150 ($M^+-2CO-2H$). These four account for over 50% of the total ion current.

Conclusion: The majority of analytical evidence indicated the sample was the desired pyracen-1,2-dione, and that the purity was >95%.

7. 1,1,1-Trichloro-3,3,3-triphenyldisilazane

The following reaction sequence was investigated as a synthetic route to this unreported disilazane.



The amine was readily prepared on reaction of triphenylchlorosilane with liquid ammonia. Treatment of the amine with n-butyllithium followed by addition of silicon tetrachloride gave a viscous oil as crude product. Attempts to purify the material by vacuum distillation at 0.05 mm were unsuccessful when the oil disproportionated to give triphenylchlorosilane at 150-170°. A high vacuum distillation at 10^{-6} mm with the temperature held below 100° gave only trace quantities of distillate.

a. Synthesis: Triphenylsilylamine was prepared by addition of an ethereal solution of 0.68 mole of recrystallized triphenylchlorosilane to liquid ammonia. Evaporation of excess ammonia and distillation of the ether gave the crude silylamine which on recrystallization from petroleum ether (b.p. 35-60°) had a m.p. of 59-60° (reported 59-60°) (Ref. 8). The infrared and NMR spectra of the product are shown in Figures 12 and 13. Final yield of triphenylsilylamine was 14.2 g (76%).

Repetition of the experiment on an 0.24 mole scale gave 52.0 g (79%) of triphenylsilylamine, m.p. 59-60°.

Treatment of 0.024 mole of triphenylsilylamine in petroleum ether (b.p. 60-90°) with a 1:1 mole ratio of n-butyllithium at room temperature gave a fine white precipitate and a mild but constant exotherm. To the mixture was added 0.024 mole of silicon tetrachloride. The mixture was refluxed for 2 hr, stirred overnight at room temperature, then filtered under nitrogen. The petroleum ether soluble material was a yellow viscous oil and weighed 2.7 g. The colorless solid collected on filtration weighed 5.5 g after drying and had an m.p. >350°. The infrared spectrum (see Figure 14) contained -NH absorption at 3400 cm^{-1} but no discernible -NH₂ band. A 1-g sample gave a basic solution when mixed with water-methanol. A flame test indicated lithium was present in the sample.

Based on the assumption the isolated solid was the unreacted lithium salt of the amine, the remaining 4.5 g was dissolved in dry tetrahydrofuran and retreated with silicon tetrachloride. During addition, a fine precipitate formed in solution. Following a 1-hr reflux period, the mixture was stirred overnight at room temperature. On attempted filtration, the fine solid passed through the fritted filter. Tetrahydrofuran was then evaporated in vacuo from the entire mixture to give 5.0 g of yellow viscous oil containing a small amount of solid. The infrared spectrum of this sample was identical to that of the 2.7 g of oil previously isolated.

A second preparation with 0.027 mole of triphenylsilylamine in tetrahydrofuran gave 8.6 g of the oil-solid mixture. Each of the three liquid products was refluxed with petroleum ether (b.p. 60-90°) and passed through a fine fritted filter. The filtrates were combined and evaporated in vacuo to give 13.5 g of oil that was free from solid. The infrared spectrum is shown in Figure 15. On standing overnight, the oil solidified.

Distillation of the solid through a short path apparatus gave 5.9 g of a light yellow liquid which solidified on cooling, b.p. 151-154° (0.05 mm), m.p. 84-89°. The infrared spectrum (see Figure 16) of the solid was identified as triphenylchlorosilane. The distillation residue consisted of 7.2 g of an intractable solid.

The recovery of triphenylchlorosilane indicates that disproportionation of the disilazane probably occurred.

The reaction was attempted on a 0.109 mole scale via the inverse addition of the lithium salt of triphenylsilylamine to silicon tetrachloride. The preparation of the lithium salt and the addition reaction were carried out at temperatures of 25-30°. GLC examination of the reaction mixture was made after standing overnight at room temperature. The data obtained, however, were inconclusive since the reaction mixture gave a single peak at a shorter retention time than either triphenylsilylamine or triphenylchlorosilane.

Tetrahydrofuran was then evaporated in vacuo at 25° and the residue stirred with petroleum ether (b.p. 60-90°). The mixture was filtered through a fine fritted filter and the filtrate was distilled under reduced pressure to give 39.7 g of light brown oil. The infrared spectrum was identical to Figure 15.

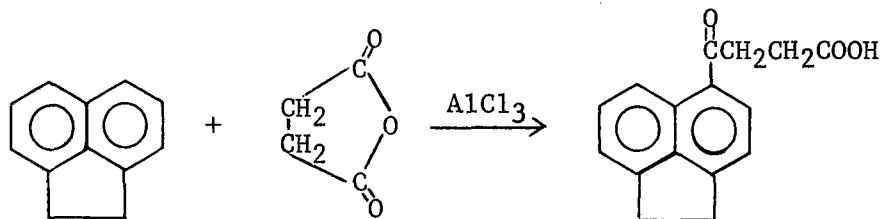
The aromatic multiplet in the NMR spectrum of the sample (see Figure 17) has the same general shape as the multiplets for both triphenylsilylamine and triphenylchlorosilane (see Figure 18). However, slight shifts in δ values occur among the spectra. The signals at low frequencies in the product spectrum are probably due to impurities.

Differential thermal analysis of the sample (see Figure 19) indicated thermal decomposition at 147-155° (corrected) and shows a series of endotherms at 333-401° (corr.) which could be expected for decomposition products. The DTA of triphenylchlorosilane (see Figure 20) gave a melting endotherm at 88-94° (corr.) and a second endotherm at 370-376° (corr.).

An attempt was made to distill a small sample of the oil using vacuum rack techniques. A vacuum of 1×10^{-6} mm was achieved; however, only trace amounts of material were collected in the Dry Ice-alcohol and liquid nitrogen traps even on heating the sample to 100° for 30 min.

8. β -(3-Acenaphthoyl)propionic Acid

This compound was prepared in 65% yield by the aluminum chloride catalyzed condensation of acenaphthene and succinic anhydride (Ref. 9).



a. Synthesis: To a stirred solution of 100 g (0.65 mole) of sublimed acenaphthene and 72 g (0.72 mole) of succinic anhydride in 600 ml of nitrobenzene was added 195 g (1.46 mole) of anhydrous aluminum chloride in small increments while maintaining the temperature below 5° . Stirring was continued at 0° for 4 hr before allowing the mixture to warm to room temperature overnight.

The reaction flask was immersed in ice water to control the temperature while 200 g of ice, 100 ml of water and 100 ml of concentrated hydrochloric acid were added in order cautiously. The reflux condenser was replaced with a high-capacity concentrator condenser and the solvent was removed from the stiff, grayish paste by steam distillation. The flask was heated during distillation to avoid water accumulation in the flask. Severe frothing was encountered as the stiff, pasty mass disintegrated into smaller particles. The yield was diminished by losses which occurred when the condenser plugged and when product was drawn back into the steam trap during a steam failure. The crude product was separated from the hydrochloric acid by filtration and returned to the flask together with 50 g of sodium carbonate monohydrate and about 1200 ml of water. The brown solution obtained by carefully raising the temperature to 90° with stirring was steam-distilled to eliminate the last traces of nitrobenzene. After filtration of the hot solution (about 1.5 liters) 100 g of sodium chloride was dissolved in the filtrate.

The fibrous salt which separated as the solution cooled in a refrigerator overnight was collected on a large Büchner funnel and was washed free of the dark mother liquor with half-saturated sodium chloride solution. The sodium salt was recrystallized from 1.2 liters of hot water using Norit decolorization. Fifty grams of sodium chloride was added to the hot solution to decrease solubility. The purified salt was dissolved in 1.2 liters of hot water and the solution was acidified. The free acid was removed by filtration, pressed dry under a rubber dam, and dried to constant weight at 70° in a vacuum oven. The yield was 107 g (65%) of β -(3-acenaphthoyl)propionic acid, m.p., $209-210^\circ$ dec. (reported m.p. $206-208^\circ$ dec) (Ref. 9).

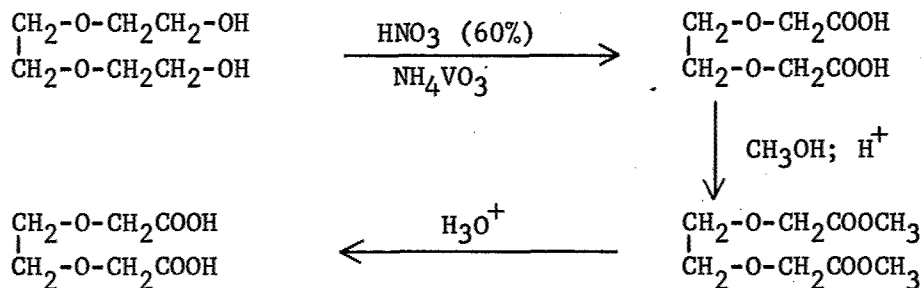
b. Physical properties: β -(3-Acenaphthoyl)propionic acid was a white powder, m.p. 209-210° dec. The infrared spectrum is reported in Figure 21.

c. Purity: The sample was of 99+% purity by elemental analysis.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.78; H, 5.50.

9. 3,6-Dioxaoctanedioic Acid

This acid was prepared by the nitric acid oxidation of triethylene glycol (Ref. 10). The crude acid was purified by preparation and distillation of the dimethyl ester (Ref. 11). Hydrolysis of the ester afforded the pure material (Ref. 12).



a. Synthesis: To 630 g of 60% nitric acid was added 1.0 g of triethylene glycol and 0.6 g of ammonium metavanadate. The solution was heated to 68° and maintained at this temperature for 2 hr. The evolution of brown fumes indicated oxidation had been initiated. The remainder (149 g) of 1 mole of triethylene glycol was added at a rate to maintain the temperature at 68-73° without external heating. The addition was completed in 2.5 hr. After an additional stirring period of 1 hr, the nitric acid was stripped under reduced pressure leaving a brown syrup. The syrup was subjected to high vacuum at 60° to remove additional volatiles. Trituration of the syrup with toluene resulted in slow solidification of the crude acid.

A solution of 140 g (0.79 mole) of crude 3,6-dioxaoctanedioic acid in 470 ml of ethylene dichloride was refluxed with 50 g (4.7 mole) of methanol and 5 ml of concentrated sulfuric acid for 16 hr. Water was then added and a phase separation was carried out. The ethylene dichloride solution was washed with 300 ml of 5% sodium bicarbonate and twice with 10% aqueous sodium chloride. The ethylene dichloride solution was then dried over magnesium sulfate and the solvent distilled in vacuo to give 103.5 g of a light amber oil. Distillation of the crude ester through a 6 in. Vigreux column gave 58.5 g (43%) of the dimethyl ester, b.p. 133-134° (2.5 mm); [reported 138-140°

(4 mm)] (Ref. 11); n_D^{25} 1.4363. The material was found to be 99% pure by GLC (0.5 m, Apiezon L, 150°, He:15 psig, FID). The infrared spectrum is shown in Figure 22.

Repetition of the procedure on a 1.41 mole scale gave an additional 159.5 g (65%) of the dimethyl ester.

A mixture of 58.5 g (0.33 mole) of dimethyl 3,6-dioxaoctanedioate and 60 ml of water with 0.6 g of Dowex 50W-X2 (cation exchange resin) was refluxed for 9 hr while the displaced methanol was removed via distillation through a 6 in. Vigreux column and a small distillation head. Excess water was then distilled in vacuo and the residue allowed to recrystallize to a white solid. The crystalline product was dried over phosphorus pentoxide at 0.1 mm for 18 hr to give 48 g (82%) (34% overall recovery for the purification) of 3,6-dioxaoctanedioic acid, m.p. 71-74.5° (differential thermal analysis, Figure 23) (reported 73-76°) (Ref. 12).

Hydrolysis of the remaining 159.5 g of the dimethyl ester by the same procedure gave an additional 120 g (74%) of purified acid.

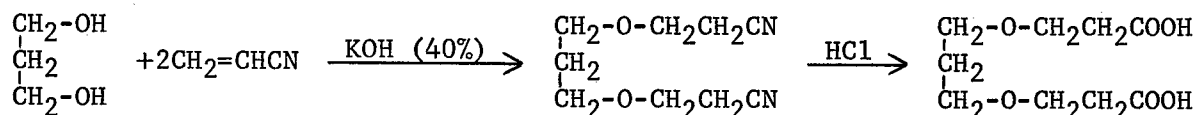
b. Physical Properties: 3,6-Dioxaoctanedioic acid was a white solid, m.p. 71-74.5°. The infrared spectrum is reported in Figure 24.

c. Purity: An elemental analysis of the sample indicated the purity to be 99+%.

Anal. Calcd. for $C_6H_{10}O_6$: C, 40.45; H, 5.66. Found: C, 40.68; H, 5.91.

10. 4,8-Dioxaundecanedioic Acid

This compound was prepared in 64% yield by acid hydrolysis (Ref. 13) of the corresponding dinitrile which was prepared by cyanoethylation of 1,3-propanediol (Ref. 14).



a. Synthesis: To a solution of 152.0 g (2.0 mole) of 1,3-propanediol and 10.7 g of 40% potassium hydroxide was added 212 g (4.0 mole) of acrylonitrile. Addition was made over 1 hr while maintaining the reaction temperature at 25-30°. After stirring for 18 hr at room temperature, the solution was acidified with 10% hydrochloric acid. Water and lower boiling

components were then removed via distillation on a rotary film evaporator, and the precipitated salts removed by filtration. After a preliminary flash distillation, the material was distilled through a 30 cm vacuum jacketed column. Final yield of 1,3-di-(2-cyanoethoxy)propane (I) was 273.6 g (75%), b.p. 134-137° (0.05 mm); [reported 165° (1 mm)] (Ref. 14). The sample was of 98.5% purity by gas liquid chromatography (GLC), (2 m 5% SF-96 on Gas Chrom Q, 75°; He: 15 psig, FID). The infrared spectrum is shown in Figure 25.

A stirred mixture of 273.6 g (1.5 mole) of 1,3-di-(2-cyanoethoxy)propane and 600 g of concentrated hydrochloric acid was gradually heated to 60°. A strong exothermic reaction occurred which brought the solution to reflux temperature. An ice bath was applied until the reaction was cooled to 75°. The solution was then stirred without heating until the reaction temperature fell below 70°. A heating mantle was then used to hold the reaction mixture at 70-75° for 3 hr and then at 100° for an additional 0.5 hr. The solution was cooled, and excess hydrochloric acid distilled on a rotary evaporator. The residue was slurried with warm acetone, the mixture was filtered, and the ammonium chloride cake was washed with additional acetone. Distillation of the acetone in vacuo left 363 g of a light yellow oil which crystallized on cooling to a white solid. Two recrystallizations from 1,200 ml of 5:1 mixture of benzene and petroleum ether (b.p. 60-90°) gave 210.0 g (64%) of 4,8-dioxaundecanedioic acid, m.p. 83.5-85.5° (differential thermal analysis, Figure 26); (reported 86-87°) (Ref. 13).

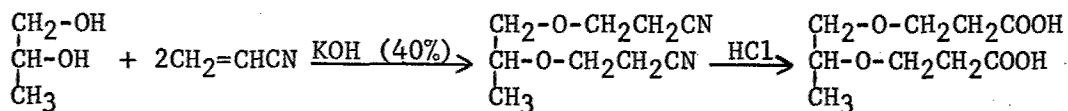
b. Physical Properties: 4,8-Dioxaundecanedioic acid was a white solid, m.p. 83.5-85.5°. The infrared spectrum is shown in Figure 27.

c. Purity: Elemental analysis indicated the sample was of 99% purity.

Anal. Calcd. for C₉H₁₆O₆: C, 49.09; H, 7.32. Found: C, 49.45; H, 7.41.

11. 5-Methyl-4,7-dioxadecanedioic Acid

This compound was synthesized by the procedure employed for the preparation of 4,8-dioxaundecanedioic acid (Refs. 13 and 14). Cyanoethylation of 1,2-propanediol followed by acid hydrolysis of the dinitrile afforded 5-methyl-4,7-dioxadecanedioic acid in 72% yield.



a. Synthesis: To a solution of 110 g (1.45 moles) of 1,2-propanediol and 7.7 g of 40% KOH was added 155 g (2.9 moles) of acrylonitrile. Addition was made over 1 hr while holding the reaction temperature at 25-35°. After stirring for an additional 18 hr at room temperature, the solution was acidified with dilute hydrochloric acid (10%) and distilled through a 6 in. unpacked vacuum-jacketed column. A total of 156.0 g (60%) of 1,2-di-(2-cyanoethoxy)propane was obtained, b.p. 143-146° (0.2 mm). The infrared spectrum is shown in Figure 28. To 156.0 g (0.87 mole) of 1,2-di-(2-cyanoethoxy)propane was added 340 g of concentrated hydrochloric acid. The solution was heated at 70-80° for 4 hr, then at 100° for 0.5 hr. After stirring at room temperature overnight, the hydrochloric acid was evaporated in vacuo to give a heavy brown syrup contaminated with solid. The mixture was stirred with warm acetone and filtered. Concentration of the acetone solution gave 200.7 g of a brown syrup.

Repeated efforts to crystallize the crude acid were unsuccessful. The crude product was dissolved in benzene and treated twice with Norit A. After evaporation of the benzene a total of 138.0 g (72%) of a light amber oil was obtained.

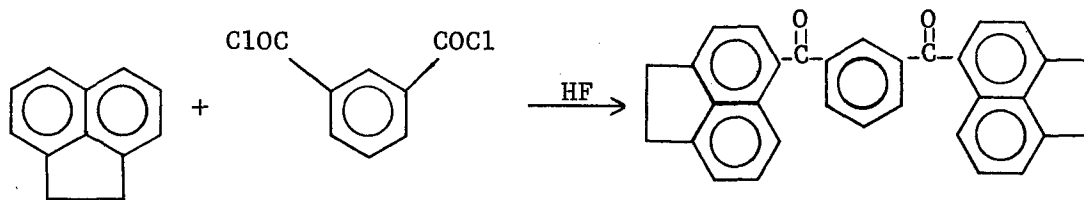
b. Physical Properties: 5-Methyl-4,7-dioxadecanedioic acid was an amber oil. The infrared spectrum is shown in Figure 29.

c. Purity: The sample was of 99% purity by elemental analysis.

Anal. Calcd. for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 48.68; H, 7.16.

12. Bis-5,5'-acenaphthenyl(1,3-phenyl)ketone

This compound was prepared in 48% yield by the hydrogen fluoride catalyzed condensation of acenaphthene and isophthaloyl chloride (Ref. 1).



a. Synthesis: A mixture of 30.8 g (0.2 mole) of recrystallized acenaphthene, 20.3 g (0.1 mole) of freshly distilled isophthaloyl chloride, and 340 g of anhydrous hydrogen fluoride was stirred at 0° in a lightly stoppered 1-liter polyethylene flask. The reaction was allowed to reach room temperature overnight. Excess hydrogen fluoride was then blown off with a nitrogen stream, and the solid residue treated with two 1,000-ml portions

of boiling 10% aqueous sodium bicarbonate. The insoluble material was then triturated with petroleum ether (b.p. 60-90°). A total of 25.8 g of light brown solid was recovered after filtering and air drying.

The reaction was repeated and an additional 26.1 g of crude product was obtained.

The combined crude products were then dissolved in 3,500 ml of refluxing ethyl acetate. The solution was decolorized with Norit A, then concentrated to approximately 750 ml and chilled. The precipitate was collected and vacuum dried at 50°. Final yield of bis-5,5'-acenaphthenyl(1,3-phenyl)ketone was 42.5 g (48% average for two runs), m.p. 187-191°, 180-184° (differential thermal analysis, Figure 31) (reported m.p. 186-190°) (Ref. 1).

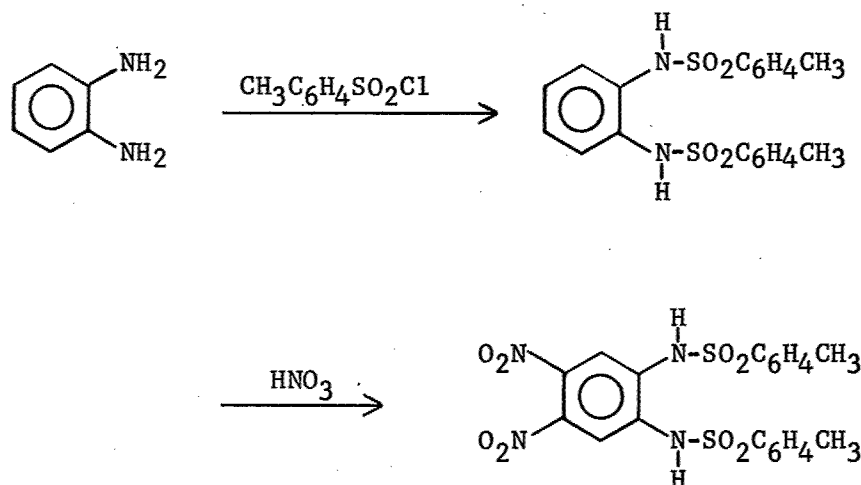
b. Physical Properties: Bis-5,5'-acenaphthenyl(1,3-phenyl)ketone was a cream colored solid, m.p. 180-184°. The infrared spectrum is shown in Figure 30.

c. Purity: The sample was 99% pure by elemental analysis.

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06. Found: C, 87.55; H, 5.36.

13. 4,5-Dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide)

This compound was prepared in a 62% overall yield by the following procedure (Ref. 15).



a. Synthesis: To a stirred solution of 114 g (1.05 moles) of o-phenylenediamine, which had been recrystallized from water with sodium hydro-sulfite and charcoal, in 750 ml of pyridine was added a solution of 404 g

(2.12 moles) of recrystallized *p*-toluenesulfonylchloride (Ref. 16) in 300 ml of pyridine. Addition was made at a rate that maintained the temperature at 60°. The mixture was stirred overnight at 60°, then cooled and added to 9.0 liters of 15% hydrochloric acid. The precipitated material was filtered and recrystallized from 3.0 liters of acetic acid. Final yield of *N,N'*-*o*-phenylenebis(*p*-toluenesulfonamide) was 406.5 g (93%), m.p. 203-205° (reported 203°) (Ref. 17).

A slurry of 310.0 g (0.75 mole) *N,N'*-*o*-phenylenebis(*p*-toluenesulfonamide) in 3470 ml of glacial acetic acid was heated to 60°. Approximately one-third of a solution of 100 ml of fuming nitric acid in 117 ml of glacial acetic acid was added rapidly to the reaction mixture. The solution turned reddish brown as an exotherm raised the temperature to 70°. The heating mantle was removed and the exotherm was allowed to subside. The heating mantle was reapplied and the remaining nitration mixture was added dropwise over 1.5 hr at 65-70°. Heating was continued for 45 min after completion of addition.

After stirring at room temperature overnight the precipitate was filtered and recrystallized from approximately 12 liters of glacial acetic acid. The recrystallized solid was dried at 80° (0.1 mm) for 6 hr.

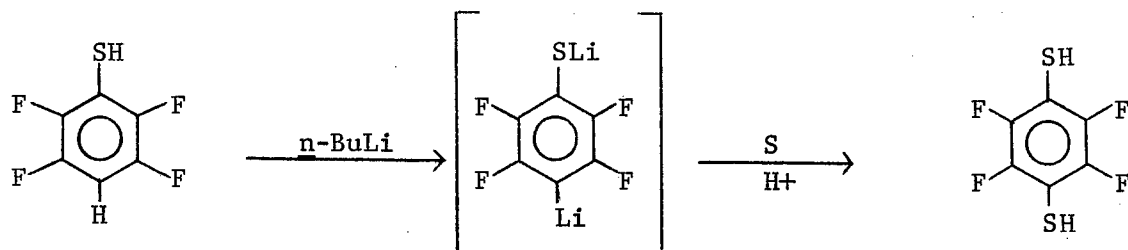
A total of 250 g (67%) of light yellow product was obtained, m.p. 245-246° (dec.) [reported m.p., 248-250° (dec.)] (Ref. 18).

b. Physical Properties: 4,5-Dinitro-*N,N'*-*o*-phenylenebis(*p*-toluenesulfonamide) was a yellow crystalline solid, m.p. 245-246° dec. The infrared spectrum is reported as Figure 32.

c. Purity: The sample was of 99+% purity by comparison of the melting point and infrared spectrum to those of a known sample of 99+% purity.

14. 2,3,5,6-Tetrafluorobenzene-1,4-dithiol

This compound was prepared by the two-step treatment of 2,3,5,6-tetrafluorothiophenol with *n*-butyllithium and elemental sulfur (Ref. 1).



a. Synthesis: A solution of 91.0 g (0.05 mole) of 2,3,5,6-tetrafluorothiophenol in 1300 ml of tetrahydrofuran was treated dropwise with 625 ml (1.0 mole) of *n*-butyllithium (1.6 M solution in hexane) while maintaining the temperature at -65°. The solution was stirred at -70° for 3 hr, then 16.0 g (0.50 g-atom) of powdered sulfur was added and the mixture was stirred overnight with slow warming from -70° to room temperature.

The reaction mixture was hydrolyzed by dropwise addition of 450 ml of 6 N hydrochloric acid. The phases were separated and the acidic aqueous phase was extracted with ether. The ether extract was then combined with the organic phase and was washed with 1100 ml of 7% potassium hydroxide. This basic aqueous phase was separated and acidified, and the amber oil which separated was combined with the ethereal phase. The ether solution was dried with magnesium sulfate and evaporated in vacuo to afford 88.8 g of an amber oil which solidified on cooling.

The solid was taken up in 800 ml of hot petroleum ether (b.p. 30-60°) and treated with charcoal. The filtrate was concentrated to approximately 300 ml and chilled. A total of 69.0 g of light yellow solid was collected by filtration.

A second experiment on the same scale gave an additional 66.0 g of crude product.

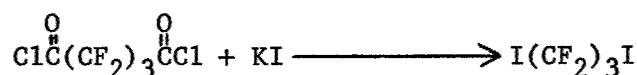
The two samples were combined and sublimed at 50-55° (0.01 mm) to give 112.0 g (56%) of white crystalline solid, m.p. 68-71° (differential thermal analysis, Figure 33), [reported m.p., 74-76° (Ref. 1); 70-72° (Ref. 19)].

b. Physical Properties: 2,3,5,6-Tetrafluorobenzene-1,4-dithiol was a white crystalline solid, m.p. 68-71°. The infrared and NMR spectra are reported as Figures 34 and 35.

c. Purity: The sample was of 99+% purity by GLC (2 m, 5% SF-96 on Gas Chrom Q, 100°, He carrier: 10 psig, FID). (See Figure 36.)

15. 1,3-Diiodohexafluoropropane

This compound was prepared in 67% yield via the high temperature reaction of potassium iodide and perfluoroglutaryl chloride (Ref. 1).



a. Synthesis: Potassium iodide (398.0 g, 2.4 mole) was dried in a 1-liter stainless steel autoclave at 150° for 3 hr at 0.2 mm Hg. The autoclave was then allowed to cool to room temperature overnight while vacuum pumping was continued.

The autoclave was charged with 166.2 g (0.60 mole) of perfluoroglutaryl chloride by drawing the liquid into the evacuated bomb. The sealed autoclave was then heated at 225-250° for approximately 4 hr. After cooling to room temperature overnight, the autoclave was carefully vented in a well ventilated area to remove the CO formed in the reaction. The purple mass was washed into a beaker with 1 liter of water and the mixture was treated with sufficient solid sodium thiosulfate to destroy excess iodine.

The mixture was extracted twice with methylene chloride and the extracts were washed with water and dried. Distillation of the solvent in vacuo at 25° afforded 164 g of a dark brown liquid.

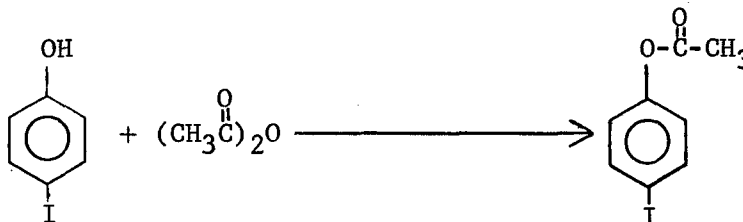
The residue was combined with the crude products isolated from an additional two reactions carried out on a 0.75 mole scale. The combined material (713.5 g) was then distilled through a short unpacked column to afford 570.5 g (67%) of 1,3-diiodohexafluoropropane, b.p. 130-132.5° (reported b.p. 131°) (Ref. 20).

b. Physical properties: 1,3-Diiodohexafluoropropane was a purple liquid, b.p. 130-132.5°. The infrared spectrum is reported as Figure 37.

c. Purity: The sample was of 99+% purity by GLC (2 m, 20% SF-96 on Chromosorb P, 100°, He carrier: 15 psig, thermal conductivity) (Figure 38).

16. 4-Iodophenyl Acetate

Preparation of this material was achieved in 94% yield on treatment of 4-iodophenol with acetic anhydride (Ref 1).



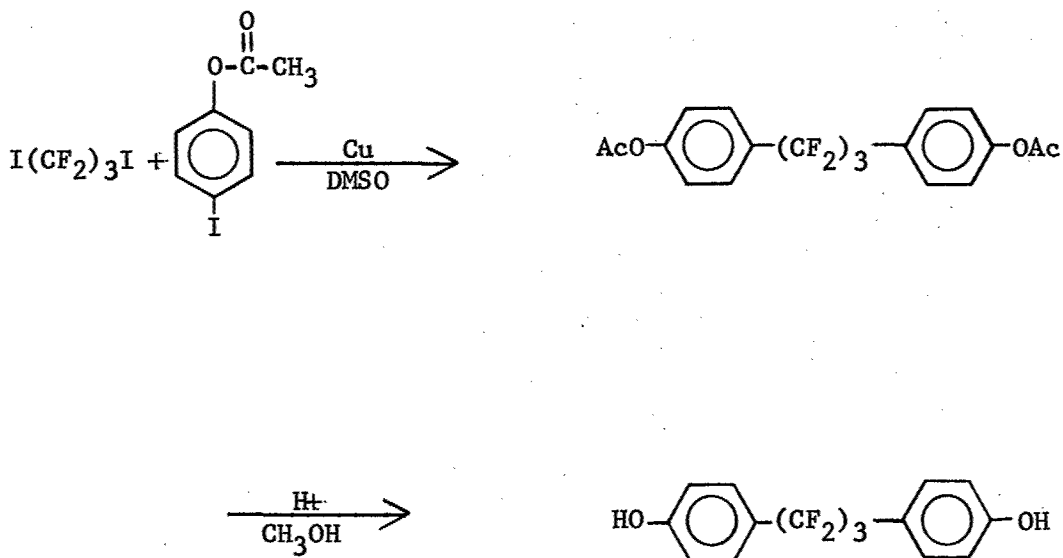
a. Synthesis: A solution of 425 g (1.93 mole) of 4-iodophenol in 800 ml of acetic anhydride was heated under reflux for 1 hr. After standing at room temperature overnight, excess acetic anhydride was distilled in vacuo and the residue distilled through a short column to afford 474 g (94%) of a colorless liquid, b.p. 78-82° (0.05 mm) [reported b.p. 72° (0.02 mm)] (Ref. 1). The liquid was seeded with a small crystal found in the distillation head. Immediate crystallization occurred. The solid had a melting point of 33-35° (reported m.p. 32-32.5°) (Ref. 21). Two additional reactions on the same scale gave 450 g (89%) and 452 g (89%) of 4-iodophenyl acetate.

b. Physical properties: 4-Iodophenyl acetate was a white solid, m.p. 33-35.5°. The infrared spectrum is reported as Figure 39.

c. Purity: The sample was of 99+% purity by GLC (2 m, 5% SF-96 on Gas Chrom Q, 140°, He carrier: 10 psig, FID) (Figure 40).

17. 1,3-Bis(4-hydroxyphenyl)hexafluoropropane

This compound was prepared in 32% yield via the copper coupling reaction of 1,3-diiodohexafluoropropane and 4-iodophenyl acetate followed by acid catalyzed hydrolysis in methanol (Ref. 1).



a. Synthesis: To a solution of 62.9 g (0.24 mole) of 4-iodophenyl acetate and 48.5 g (0.12 mole) of 1,3-diiodohexafluoropropane in 240 ml of dimethylsulfoxide was added 61.0 g of copper powder. The mixture was heated at 120-130° for 4 hr under a nitrogen atmosphere. The mixture was cooled to room temperature, then poured into a separatory funnel containing 2 liters of water and 2 liters of ethyl ether. The mixture was shaken and the phases separated and filtered. The aqueous phase was extracted with additional ether and the extract combined with the original ether layer. The ether phase was washed three times with water, dried with sodium sulfate, and treated with activated charcoal. Evaporation in vacuo gave a light yellow oil which crystallized on standing.

The solid was dissolved in 300 ml of methanol and treated with 12 ml of concentrated hydrochloric acid. The solution was refluxed for 15 min, then evaporated in vacuo to afford a light brown solid.

The solid product was combined with the material isolated from two additional reactions and placed in a 1-liter capacity Soxhlet thimble. The material was then extracted for 8 hr with heptane. The purple heptane solution was cooled to ice bath temperatures and filtered. Because of apparent decomposition of a portion of the product, the thimble had disintegrated, so the remaining crude product and thimble fragments were placed in a double thickness thimble and extracted for an additional 8 hr. The heptane was again cooled, filtered, and the solid was combined with the product isolated in the first 8 hr. The combined solids were taken up in 1500 ml of hot benzene and decolorized with activated charcoal. The solution was evaporated to dryness to afford 45 g of a light tan colored solid m.p. 140-147°.

The solid was taken up in approximately 600 ml of hot chloroform treated with charcoal and chilled. A first crop of 32 g of white solid was isolated. On concentration and cooling of the filtrate an additional 7.3 g of product was obtained for a total yield of 39.3 g (32.5%) of 1,3-bis(4-hydroxyphenyl) hexafluoropropane, m.p. 148-150.5° (reported m.p. 150-151°) (Ref. 1).

Two additional reactions were carried out on the same scale. The combined crude material, however, was not heptane extracted. Recrystallization and decolorization from chloroform gave 25.0 g (32%) of product in two crops, m.p. 152-154°.

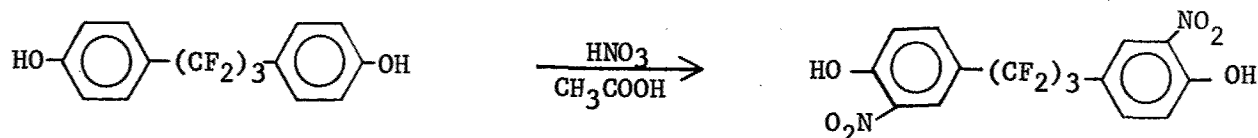
b. Physical properties: 1,3-Bis(4-hydroxyphenyl)hexafluoropropane was a white solid, m.p. 152-154°. The infrared spectrum is reported in Figure 41.

c. Purity: The sample was of 99+% purity based on elemental analysis.

Anal. Calcd. for $C_{15}H_{10}F_6O_3$: C, 53.58; H, 3.00. Found: C, 53.75; H, 3.01.

18. 1,3-Bis(3-nitro-4-hydroxyphenyl)hexafluoropropane

This compound was prepared in 51% yield by nitration of 1,3-bis(4-hydroxyphenyl)hexafluoropropane (Ref. 1).



a. Synthesis: A stirred solution of 7.8 g (0.023 mole) of 1,3-bis(4-hydroxyphenyl)hexafluoropropane in 100 ml of glacial acetic acid was treated with 13 ml of concentrated nitric acid. The solution was then heated to 40° by water bath. The solution became an intense red and an exotherm occurred which was held at $45\text{--}50^\circ$ by ice bath. After the reaction had subsided, the solution was heated by oil bath at 45° for 1.5 hr. The solution was cooled and then diluted with an equal volume of water. The precipitate was filtered and washed with additional water. Recrystallization of the yellow solid from ethanol with charcoal decolorization afforded 5.0 g (51%) of product, m.p. $122.5\text{--}124.5^\circ$ (DTA, Figure 42) [Reported m.p. $132\text{--}133^\circ$ (Ref. 1)]. A second experiment on a fourfold scale gave an additional 20.9 g of 1,3-bis(3-nitro-4-hydroxyphenyl)hexafluoropropane.

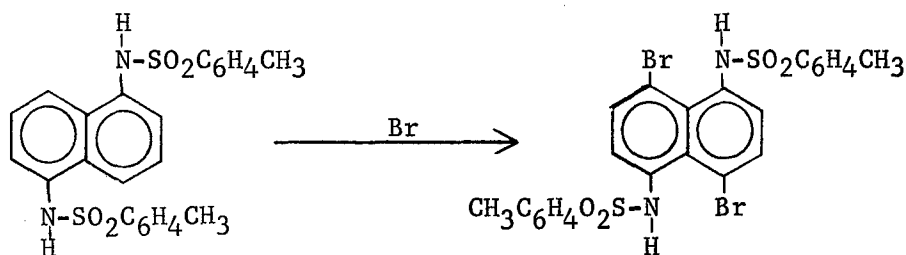
b. Physical properties: The material was a yellow solid which had a melting point of $122.5\text{--}124.5^\circ$. The infrared spectrum is shown as Figure 43.

c. Purity: The sample was shown to be of 99+% purity based on elemental analysis:

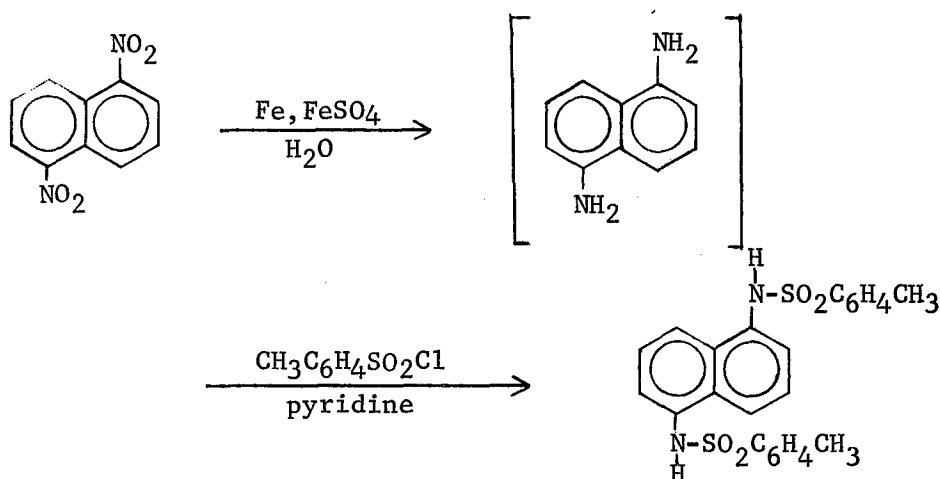
Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{F}_6\text{N}_2\text{O}_6$: C, 42.27; H, 1.89; N, 6.27. Found: C, 42.10; H, 1.72; N, 6.27 (Galbraith Labs). C, 41.98; H, 1.81; N, 6.43 (MRI In-house).

19. 4,8-Dibromo-1,5-bis(p-toluenesulfonamido)naphthalene

Preparation of this compound was achieved by direct bromination of 1,5-bis(p-toluenesulfonamido)naphthalene (Refs. 22 and 23).



a. Synthesis: Preparation of the intermediate was attempted by reduction of 1,5-dinitronaphthalene with iron and ferrous sulfate followed by tosylation of the amino groups (Refs. 23 and 24).



However, when one experiment was carried out according to literature procedure the reaction exothermed uncontrollably. A commercial source of 1,5-diaminonaphthalene was found, and the reduction procedure was abandoned. The direct tosylation of the diaminonaphthalene proceeded smoothly to the desired 1,5-bis(p-toluenesulfonamido)naphthalene. Bromination of this compound gave the final product in 36% yield.

(1) Via reduction and tosylation of 1,5-dinitronaphthalene (attempted):

A mixture of 200 g (0.92 mole) of 1,5-dinitronaphthalene, 60 g of iron powder, 60 g of ferrous sulfate and 2 liters of water was gradually heated toward reflux temperature. At approximately 70°, the reaction exothermed violently, and spewed the reaction mixture out of the flask. No further investigation of the reaction was attempted.

(2) Via direct tosylation of 1,5-diaminonaphthalene: A slurry of 100 g (0.7 mole) of 1,5-diaminonaphthalene in 500 ml of pyridine was heated

to 55°. To the purple mixture was added a solution of 265 g (1.4 mole) of p-toluenesulfonyl chloride in 300 ml of pyridine at a rate which maintained the temperature at 55-60°. With approximately 75 ml of the tosyl chloride solution left to be added, the tosylated amine precipitated from solution. Since the mixture could not be stirred, it was heated to 115° and the precipitate dissolved before addition was completed. The solution was heated for an additional 10 min, then transferred hot to a beaker, diluted with approximately 500 ml of water, and allowed to cool overnight. The precipitate was filtered and recrystallized from pyridine. The recrystallized product was then slurried with 500 ml of cold pyridine and 500 ml of ether. The pink solid was dried in vacuo at 120° for several hours. Final yield of 1,5-bis(p-toluenesulfonamido)naphthalene was 210 g (65%), m.p. 322-324° (dec.) [reported m.p. 318° (dec.)] (Ref. 22). The infrared spectrum is reported in Figure 44.

A slurry of 100 g of 1,5-bis(p-toluenesulfonamido)naphthalene in 3 liters of glacial acetic acid was heated to 95° and treated dropwise with 40 ml of bromine. The slurry was heated an additional 10 min after completion of addition, then cooled and filtered. The silver colored solid was slurried with 2 liters of boiling anhydrous ethanol and filtered. The solid was then combined with the product isolated from an identical reaction and extracted in a Soxhlet extractor with anhydrous ethanol for 4 hr, washed with ether, and dried in vacuo to afford 96.4 g of silver-gray product, m.p. 249-250° (dec.) [reported m.p. 248° (dec.)] (Ref. 22). The average yield for the two reactions was 36%.

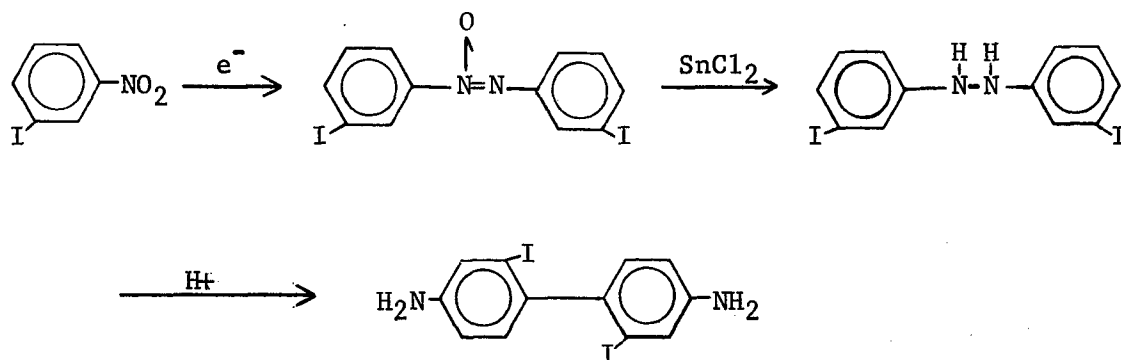
b. Physical properties: 4,8-Dibromo-1,5-bis(p-toluenesulfonamido)naphthalene was a silver-gray powder, m.p. 249-250° dec. The infrared spectrum is reported as Figure 45.

c. Purity: An elemental analysis gave acceptable values for hydrogen, nitrogen, and sulfur. However, the carbon value was high and the bromine value low.

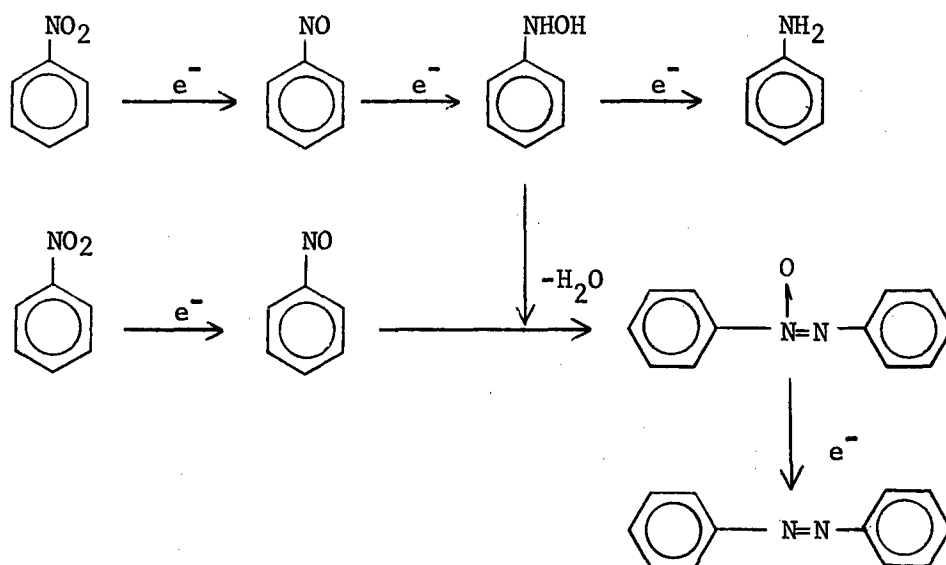
Anal. Calcd. for $C_{24}H_{20}O_4N_2Br_2S_2$: C, 46.16; H, 3.23; O, 10.25; N, 4.49; Br, 25.60; S, 10.27. Found: C, 47.35; H, 3.25; N, 4.69; Br, 20.91; S, 10.50.

20. 2,2'-Diiodobenzidine

This compound was synthesized from m-iodonitrobenzene by electrochemical reduction to 3,3'-diiodoazoxybenzene. The azoxy compound is chemically reduced to the corresponding hydrazo compound which then undergoes the benzidine rearrangement to form 2,2'-diiodobenzidine (Ref. 25).



The electrolytic reduction of m-iodonitrobenzene probably follows the scheme proposed (Ref. 26) for the electrolytic reduction of nitrobenzene which is presented as follows.



Because of the multiplicity of products that can be formed in this sequence, it is essential that the proper conditions be employed to assure production of the desired azoxy compound. The most important factors to be considered are: (1) catholyte and anolyte; (2) current density at the cathode; and (3) cathode material. The literature procedure for the preparation of this compound (Ref. 25) fully describes the first two of these factors. However,

the cathode material was not identified. It has been reported that in order to produce a good yield of azoxy compound, the cathode must be a material of low overpotential such as nickel or platinum (Ref. 27). From an economic standpoint, it was decided that nickel should be investigated first.

A series of experiments was run using nickel wire as the cathode. Several lengths of wire were used with corresponding adjustments in applied voltage so as to operate at the recommended current density of 0.05 amp/cm^2 . However, in all of these runs, the product yield was considerably lower than the reported (90%) and appreciable quantities of a material which was thought to be the hydroxylamine were isolated. It was concluded that the overpotential of nickel was such that the nitroso intermediate was further reduced before it had time to react with a molecule of hydroxylamine to form the azoxy compound. Platinum was then employed as the cathode material and more favorable results were obtained.

a. Synthesis: In a typical experiment 30.0 g (0.12 mole) of m-iodonitrobenzene was dissolved in a solution of 493 ml of 95% ethanol and 87 ml of water. The solution was placed in a porous battery cup (Coors No. 70008; 79 mm diameter x 177 mm height) which in turn was placed in a 2-liter beaker containing approximately 600 ml of cold saturated sodium carbonate as anolyte. The cathode was a piece of 5-mil platinum foil (1 x 5 in.) which was attached to a lead from a 5-amp capacity DC power source. The anode was a 2-ft length of 25-mil nickel wire wound several times inside the walls of the glass beaker. The entire setup was heated by a hot plate to 75° . The catholyte was stirred magnetically and current was adjusted to 3 amps (calculated amperage output to achieve a current density of 0.05 amp/cm^2 of cathode). During the course of the reaction the amperage increased; therefore, it was necessary to periodically readjust the applied voltage of the DC source to maintain the 3-amp level. It was also necessary to periodically replenish the catholyte by adding additional 95% ethanol. After 3.5 hr, hydrogen evolution was apparent and the catholyte was poured into a beaker and cooled. The orange precipitate was collected by filtration and oven-dried in vacuo at 70° . Crude yield of 3,3'-diiodoazoxybenzene was 23.0 g (85%). The crude product is pure enough to use directly in the preparation of 2,2'-diiodobenzidine; however, on recrystallization from glacial acetic acid, a sample had a melting point of $120\text{--}122^\circ$ (reported m.p. 120°) (Ref. 25). The infrared spectrum is shown in Figure 46.

A total of 18 additional reactions were carried out to afford 435 g (89% average yield) of 3,3'-diiodoazoxybenzene.

A second series of 20 runs was carried out using Coors Electrolytic Cups No. 70009. These cups are heavy walled, and thus are not as susceptible to collapse after several runs as are the smaller cups (No. 70008). (Handling of the No. 70009 cups is more convenient if they are shortened by 7-8 cm before use.)

The 20 reactions gave a total of 429 g of 3,3'-diiodoazoxybenzene for an average yield of 80%.

A slurry of 70.0 g (0.15 mole) of 3,3'-diiodoazoxybenzene in 750 ml of ether was added portion-wise to a solution of 225 g (1.2 mole) of SnCl_2 in 750 ml of concentrated HCl . The mixture was stirred at room temperature for 4 days during which time the solid changed from yellow to white. The ether was then distilled in vacuo and the solid was filtered.

The white paste was dissolved in 20% ethyl alcohol and neutralized with ammonium hydroxide. The white precipitate was filtered and then extracted with 1 liter of hot absolute ethyl alcohol. The hot alcohol extract was diluted with water until cloudiness occurred. On cooling, a white powder precipitated which was collected by filtration and vacuum oven dried. The yield of crude 2,2'-diiodobenzidine was 16.8 g, m.p. 138-150°.

The material was combined with the crude products isolated from five additional reactions to afford 98.0 g of material which was recrystallized from benzene. A total of 59.0 g (14% average yield) of 2,2'-diiodobenzidine was obtained which had a melting point of 167.5-169° (DTA, Figure 47) (reported m.p. 169°) (Ref. 25).

An additional six runs carried out with a total of 429 g (0.95 mole) of 3,3'-diiodoazoxybenzene gave 80.0 g (19% average yield) of 2,2'-diiodobenzidine, m.p. 167-169° (DTA).

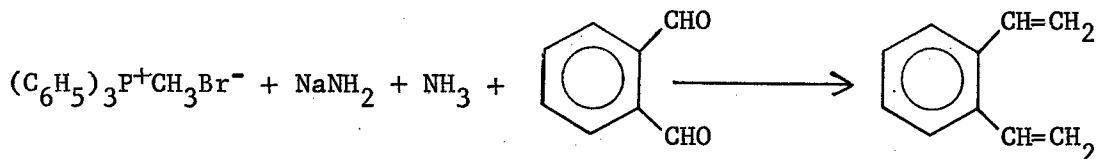
b. Physical properties: The material was a white powder, m.p., 167.5-169°. The infrared spectrum is reported in Figure 48.

c. Purity: Elemental analysis indicated the sample was of 99+% purity.

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{I}_2$: C, 33.05; H, 2.31; N, 6.43; Found: C, 33.13; H, 2.53; N, 6.24.

21. o-Divinylbenzene

Preparation of this compound was achieved via the following literature procedure (Ref. 28).



Because the procedure employs large volumes of liquid ammonia, an initial series of exploratory experiments was attempted in an effort to develop a procedure more conducive to preparation of large quantities of product.

It was found that n-butyllithium is a common reagent in reactions of this type (Ref. 29). Therefore, several experiments were carried out with this reagent in different reaction solvents, but yields were never greater than 9%.

The first attempt to prepare the compound employed n-butyllithium addition to a phosphonium bromide suspension in tetrahydrofuran. Disappearance of the salt followed by appearance of an orange color indicated that the Wittig salt had been prepared. However, after addition of phthaldehyde and work-up according to the literature procedure, only an intractable oil was obtained. Attempted flash distillation at 0.1 mm gave no product.

Three reactions using dry ethyl ether as solvent were carried out, and in each case the desired product was isolated. Solvent ratios and reaction times were varied, but the best yield obtained was 9%.

A final reaction with n-butyllithium was then carried out with several procedure modifications employed in the preparation of olefins via Wittig reactions (Ref. 30). Instead of reaction times of 2-3 hr at reflux temperature, the reaction was water quenched after 10 min at room temperature. Hydroquinone was employed as a stabilizer in all work up steps, and a final hexane extraction was employed to separate the product from by-product salts before distillation.

By utilizing these changes, the final yield of product was increased to 25%. However, the yield was not high enough to justify use of the n-butyllithium procedure in large scale preparations.

Investigation of the literature procedure was then carried out. A 0.28 mole scale reaction (tenfold scale-up from literature procedure) was conducted using liquid ammonia and sodium amide to prepare the Wittig salt. The literature procedure was followed as closely as possible, but final yield of product was only 7%.

A second reaction was then carried out on a 0.14 mole scale. Sodium amide was prepared in situ by addition of hydrated ferric nitrate and sodium to liquid ammonia. On work-up, hydroquinone was used in all steps to stabilize the product; and the hexane extraction procedure was employed to eliminate contaminating salts before distillation. Flash distillation afforded o-divinylbenzene in 74% yield.

a. Synthesis: To 1.5 liter of liquid ammonia was added approximately 0.3 g of ferric nitrate hexahydrate. A small portion (~ 1 g) of sodium pellets was added, and the mixture was stirred until a black precipitate had formed. The remainder of 7.9 g (0.34 mole) of sodium pellets was then added portion-wise over a period of 20-30 min. A Dry Ice alcohol condenser was employed to limit the loss of ammonia during addition.

The mixture was stirred until the blue color had dissipated and the solution became gray-black in appearance. Methyltriphenylphosphonium bromide (98.2 g, 0.275 mole) was added to the stirring solution. The yellow-green solution was then heated by steam bath to evaporate the ammonia. The solid residue was dissolved in 1 liter of anhydrous ether and refluxed for 0.5 hr. After the mixture was cooled to room temperature, 18.76 g (0.14 mole) of o-phthaldehyde in 500 ml of ether was added dropwise over 0.5 hr. The mixture was stirred at reflux temperature for 2 hr, cooled and filtered. Hydroquinone was added to the filtrate, and the ether was then distilled in vacuo at 25°. The liquid residue was then shaken with 500 ml of hexane. The hexane solution was decanted from the amorphous solid residue and treated with additional hydroquinone. The hexane solution was concentrated at 25° to approximately 250 ml and then gravity filtered to remove precipitated salts. The filtrate was then further concentrated to afford a light amber oil. The oil was distilled over hydroquinone through a Claisen head into a dry-iced receiver. Final yield of o-divinylbenzene was 12.3 g (74%), b.p. 45-50° (0.05 mm), [reported b.p. 75-78° (14 mm)] (Ref. 28).

An additional eight reactions on a 0.28 mole scale gave 159.0 g (60%) of twice distilled product, b.p. 50° (0.075 mm).

b. Physical properties: o-Divinylbenzene was a colorless liquid, b.p. 50° (0.075 mm), n_D^{29} 1.5752. The infrared spectrum is reported as Figure 49.

c. Purity: The sample was 98% pure via analysis by GLC (2 m, 5% SF-96 on Gas Chrom Q, 125°, He carrier: 8 psig, FID). See Figure 50.

22. Perfluoro-n-octyl Iodide

Two samples of "perfluoralkyl iodide" mixtures were supplied by the Materials Laboratory for separation and purification of the perfluoro-n-octyl iodide component. The samples represented different lots of a product obtained from Thiokol Corporation.

a. Thiokol Lot XP79-3-3B: The 388 g sample as received, was a complex mixture containing ~ 78% of the desired perfluoro-n-octyl iodide by GLC (2 m, 20% SF-96 on Chromosorb P, 80°, He carrier: 10 psig, FID) (Figure 51).

The material was purified in two batches by a series of three distillations through a Nester-Faust autoannular spinning band distillation system in the following manner: the first distillation [A] yielded a pre-cut (A_1), a mid-cut (A_2) and a post-cut (A_3); in the second distillation [B], the pre-cut (A_1) was redistilled to yield a pre-cut (B_1), a mid-cut (B_2), and a post-cut (B_3); and in the third distillation [C], mid-cut (A_2) and mid-cut (B_2) were combined and distilled to yield a pre-cut (C_1), a mid-cut (C_2), and a post-cut (C_3).

After the final distillation [C], selected cuts were recombined to afford three final fractions:

1. A lower boiling fraction, ($B_1 + C_1$) = 29.5 g.
2. A product fraction, (C_2) = 180.5 g, b.p. 108-110°/200 mm.
3. A higher boiling fraction, ($A_3 + B_3 + C_3$) = 57.0 g.

The product fraction (2), was analyzed by GLC (conditions listed above) using both flame ionization (FID) and thermal conductivity (TC) detection systems. Analysis via FID indicated 95% purity, while the analysis via TC indicated 97.5% purity. The chromatograms of the product fraction and fractions 1 and 3 are shown in Figures 52, 53, and 54. The infrared spectrum of the product fraction is shown in Figure 55.

A mass spectrum of the product fraction was obtained to confirm that the major component of the original mixture was indeed perfluoro-n-octyl iodide. The mass spectrum was in good agreement with the proposed structure (see Table I).

b. Thiokol Lot F-33-31-HS: A total of 897.7 g of purified perfluoro-n-octyl iodide was obtained by spinning band distillation of this sample using a Nester-Faust autoannular distillation system.

The alkyl iodide mixture as supplied by Thiokol contained 84% of the desired perfluoro-n-octyl iodide by GLC on 2 m, 20% SF-96 on acid-washed Chromosorb P, 80°, He carrier: 15 psig, thermal conductivity (Figure 56). Because the sample was much less complex than Lot XP7903-3B, a single distillation of a particular batch gave the desired perfluoro-n-octyl iodide in 98% purity.

The perfluoro-n-octyl iodide was distilled and forwarded to the Materials Laboratory in three batches of 59.0 g (98.5% purity), 188.3 g (98.6% purity), and 650.4 g (98.6% purity). A typical gas chromatogram of purified material is shown in Figure 57. Also provided to the Materials Laboratory were 152.7 g of a lower boiling fraction and 110.5 g of distillation residue. Gas chromatograms of these samples are shown in Figures 58 and 59.

TABLE I

MASS SPECTRAL DATA ON PERFLUORO-n-OCTYL IODIDE*

<u>m/e</u>	<u>Relative Abundance (%)</u>	<u>Tentative Assignment</u>
546	9.97	M \oplus , $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{I}$ \oplus
420	3.69	
419	43.30	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2$ \oplus
381	5.45	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF=CF}$ \oplus
331	8.35	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF=CF}$ \oplus
281	2.97	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF=CF}$ \oplus
269	2.92	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2$ \oplus
239	4.88	
231	8.28	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF=CF}$ \oplus
227	5.84	$\text{ICF}_2\text{-CF}_2$ \oplus
219	23.36	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2$ \oplus
208	2.94	
181	12.07	$\text{CF}_3\text{-CF}_2\text{-CF=CF}$ \oplus
177	46.60	ICF_2 \oplus
170	2.92	
169	79.66	$\text{CF}_3\text{-CF}_2\text{-CF}_2$ \oplus
162	2.74	
158	1.83	
150	1.52	
132	2.14	
131	48.39	$\text{CF}_3\text{-CF=CF}$ \oplus
128	2.92	
127	46.82	I \oplus
119	79.66	$\text{CF}_3\text{-CF}_2$ \oplus
112	2.14	
101	2.60	
100	24.10	$\cdot\text{CF}_2\text{-CF}_2$ \oplus
93	5.84	
85	8.37	
81	4.18	
70	3.06	
69	100.00	CF_3 \oplus

* 95-97.5 Mole % pure.

23. Perfluoro-n-decyl Iodide

A total of 579.5 g of this compound of 98.8% purity was obtained by distillation of a decyl iodide mixture (designated Thiokol Lot No. XP-8056-4B) supplied by the Materials Laboratory. The starting mixture was found to contain one high-boiling and two low-boiling volatile impurities by GLC (2 m, 20% SF-96, on Chromosorb P, 115°, He carrier: 10 psig, FID) (Figure 60). Purity was assayed at approximately 97%.

An initial attempt to purify a small sample by distillation through an unpacked column gave colorless material, b.p. 105° (45 mm), but no fractionation of the lower-boiling contaminants was obtained. The higher boiling contaminant remained in the distillation residue.

An attempt to fractionate the mixture using a Nester-Faust autoannular spinning band distillation system failed when the compound crystallized in the column and froze the band. Bromobenzene was added to the pot material in an attempt to preheat the column above the melting point of the decyl iodide. However, the material codistilled and/or sublimed under these conditions.

Several attempts were made to remove the low-boiling impurities by washing the mixture with petroleum ether and with bromobenzene. Although the extraction removed most of the impurities, it also caused unacceptable loss of the desired product. Recrystallization of the mixture from ether, benzene, or chlorobenzene gave little fractionation of the material.

a. Preparation acceptable: Purification was finally obtained by distillation of the mixture through a 10-plate Oldershaw column which was warmed with heating tapes and infrared lamps. In this way the mixture was fractionated into the following cuts:

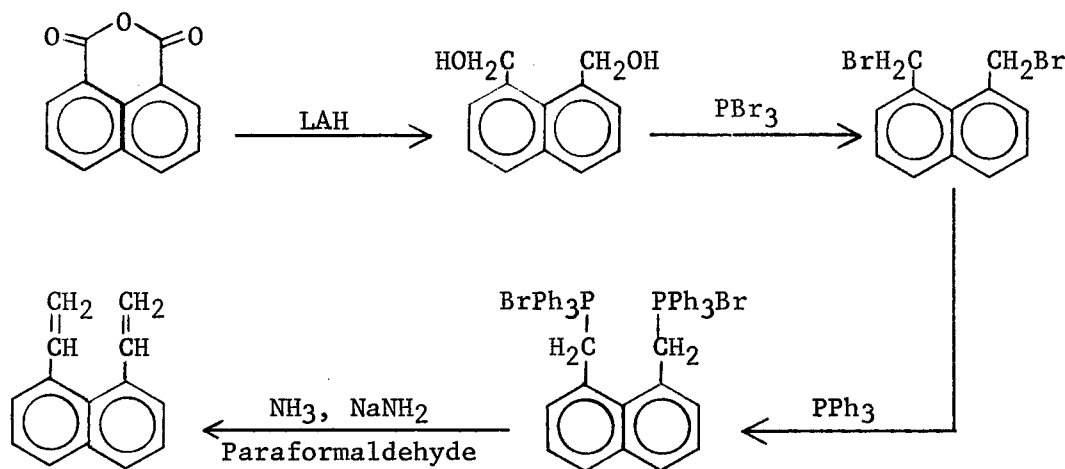
Lower-boiling fraction	36.1 g
Perfluoro-n-decyl iodide (b.p. 105-106°/15 mm)	579.5 g
Distillation residue	89.7 g

b. Physical properties: Perfluoro-n-decyl iodide was a pink solid, m.p. 62-64.5° (DTA, Figure 61). The infrared spectrum is shown in Figure 62.

c. Purity: The sample was of 98.8% purity by GLC (Figure 63). The low-boiling fraction and distillation residue contained 97.9% and 82.8% of perfluoro-n-decyl iodide respectively. The gas-liquid chromatograms of these two fractions are reported in Figures 64 and 65.

24. 1,8-Divinyl-naphthalene

Preparation of this compound has been reported via the following synthetic route (Ref. 32).



Chemical Samples Company, Columbus, Ohio, was subcontracted to prepare two samples of 1,8-divinyl-naphthalene.

Their first attempt to synthesize the desired product by the literature procedure outlined above was unsuccessful. They inadvertently prepared and submitted a sample of material (Sample No. 1) which upon characterization in our laboratories was identified as 1,8-dimethylnaphthalene.

It was suggested to Chemical Samples Company that hydrolysis had occurred during the Wittig step to the final product. Their laboratories then altered the last-step procedure and used *n*-butyllithium in ethyl ether to prepare the Wittig salt and took precautions to generate dry formaldehyde.

Two subsequent samples (Samples Nos. 2 and 3) prepared by this modification were found to be the desired 1,8-divinyl-naphthalene and of acceptable purity.

Results of characterization and purity assay for each sample are summarized in Table II and described individually as follows:

a. Sample No. 1: This lot of 44.0 g was found to have a melting point of 56-58° which was higher than any reported in the literature. Further characterization via infrared (Figure 66), NMR (Figure 67), and mass spectroscopy gave results which verified that the sample was not 1,8-divinyl-naphthalene. Investigation of the literature indicated the sample was

TABLE II

COMPARISON OF DATA SUPPORTING IDENTIFICATION OF 1,8-DIMETHYLNAPHTHALENE
(References in Parentheses)

	MRI Data on C.S.C. Sample	Literature Values	
		1,8-Divinyl-naphthalene MW 180	1,8-Dimethylnaphthalene MW 156
Melting point, °C	56-58	47-47.5 (31) 44-46 (32) 46-47 (34)	63 (35)
Infrared cm ⁻¹	768 and 810 (strong)	908, 988, 1628 (31) 908, 925, 998 (32) 908a/ (33)	773 and 814 (strong) (36)
NMR δ	x H multiplets 7.85-7.15 x H {singlet 3.3b/ singlet 2.80	8H 7.85-7.15 (32) 4H 6.70-6.60 (32)	<div> multiplets 7.80-7.10 singlet 2.86 </div> (37)
Mass m/e	Major 156, 141 Trace 180, 179, 168, 165	<div> 180 (M⁺, 66%) 179 (M-H, 64%) 178 (M-H₂, 24%) 166 (M-CH₂, 17%) 165 (M-CH₃, 100%) </div> (32)	<div> Major peaks expected: 156 for M⁺, 141 for M-CH₃ </div>

a/ The disappearance of this 908 peak was used to follow the course of a photochemical reaction.

b/ This low intensity peak amounting to only 7% of the total peak area is likely due to an impurity.

1,8-dimethylnaphthalene. Table II compares the experimental data with known literature values for 1,8-divinylnaphthalene and 1,8-dimethylnaphthalene.

The sample was not accepted, and was returned to the supplier.

b. Sample No. 2: A second lot of 100 g was found to have an acceptable melting point of 47-49°. Purity was assayed at 99+% by GLC (2 m, 5% SF-96 on Gas Chrom Q, 175°, He carrier: 15 psig, FID). The gas chromatogram is set forth as Figure 68.

Infrared and NMR spectral data were in agreement with literature values and are shown in Figure 69 and 70.

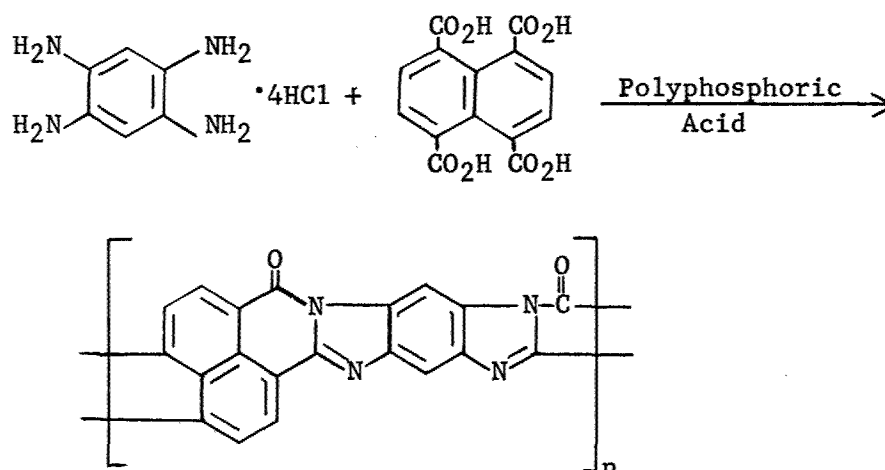
c. Sample No. 3: A third sample of 500 g was found to be acceptable. The material had a melting point of 46-48.5°. Infrared and NMR spectral data were in agreement with reported literature values and are shown in Figures 71 and 72. The sample was of 99+% purity by GLC (2 m, 5% SF-96 on Gas Chrom Q, 175°, He carrier: 12 psig, FID) (Figure 73).

25. 2,3,5,6-Tetrafluorothiophenol

A 250.0 g sample of this material was purchased from Bristol Organics Limited, Bristol, England. The sample was of 99% purity by GLC; (2 m 5% SF-96 on Gas Chrom Q, 75°, He carrier: 15 psig, thermal conductivity detector). (Figure 74). The infrared spectrum shows the presence of the -SH absorption at 2580 cm^{-1} (see Figure 75). The sample was deemed acceptable and was forwarded to the Materials Laboratory.

26. Poly[(7-oxo-7H,10H-benz[de]imidazo-[4',5':5,6]-benzimidazo[2,1-a]-isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL Polymer)

Previous efforts to prepare high-molecular weight BBL polymer by a method supplied by the Materials Laboratory (Ref. 1) which is similar to a method described in the literature (Ref. 38) gave only low molecular weight polymer (Ref. 39).



Attempts to modify the procedure by using 1,4,5,8-naphthalene-tetracarboxylic 1:8,4:5-dianhydride (NTDA) in place of the corresponding acid (NTCA) were also unsuccessful in preparing material of acceptable intrinsic viscosity (Ref. 39).

Celanese Research Company, Summit, New Jersey, was subcontracted to prepare a sample of BBL polymer with a minimum intrinsic viscosity of 1.0 dl/g.

Their initial attempts to synthesize BBL involved reaction of NTDA with 1,2,4,5-tetraaminobenzene tetrahydrochloride in the following molten Lewis Acid Salts: SbCl_3 , BiCl_3 , AlCl_3 , $\text{ZnCl}_2/\text{SnCl}_2$ eutectic and several other eutectic mixtures. Only black tars which gave low intrinsic viscosities were obtained. Similar reactions with free tetraamine also failed.

a. Synthesis: A sample of BBL was prepared using NTDA when SbCl_3 was employed in catalytic amounts with polyphosphoric acid as the solvent. The tetraamine hydrochloride was added to the polyphosphoric acid and heated at 100° for 4 hr. At the end of 4 hr, a stoichiometric amount of NTDA was added to the reaction along with 0.88 mole of SbCl_3 per mole of monomer. The entire mixture was heated to 190° over a 4 hr period, then held at that temperature for 18 hr. The solution became very thick and cherry red during this heating period. The solution was then poured in methanol and BBL precipitated in long fibrous strands. The polymer was filtered, washed several times with water and dried.

b. Sample before purification: A 5.2-g sample of BBL polymer (designated 19273-34) was received from Celanese Research Company. The sample was reported to have an intrinsic viscosity of 2.0. The infrared spectrum is shown in Figure 76.

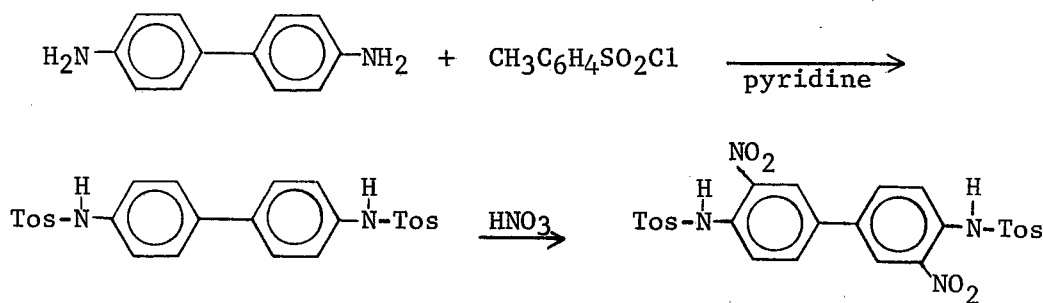
However, a viscosity determination carried out in our laboratories gave results which are characteristic of polyelectrolyte behavior (Table III). A plot of the viscometric data (see Figure 77) could not be extrapolated to obtain a value for the intrinsic viscosity.

c. Sample after purification: A 2.5-g portion of the Celanese material was dissolved in 200 ml of methanesulfonic acid. The solution was filtered through a medium porosity sintered glass filter, then dripped slowly into 1500 ml of stirred distilled water. The reprecipitated polymer was filtered and then reslurried with an additional 1500 ml of water and twice with 500 ml of anhydrous methyl alcohol. A total of 2.0 g (80% recovery) of polymer was obtained after drying for 18 hr at 80°.

The purified sample of BBL polymer was then diluted to standard concentrations of 0.1, 0.25, 0.4 and 0.5 g/dl. Viscometric data for these concentrations are reported in Table III. Extrapolation of the plotted data gave an intrinsic viscosity value of 1.38 (see Figure 78). The infrared spectrum is reported in Figure 79.

27. 3,3'-Dinitro-N,N'-di-p-toluenesulfonyl Benzidine

This compound was prepared by nitration (Ref. 40) of tosylated benzidine (Ref. 41).



a. Synthesis: To 25.0 g (0.135 mole) of benzidine (J. T. Baker reagent grade) in 200 ml of pyridine at 40° was added a solution of 51.5 g (0.27 mole) of *p*-toluenesulfonyl chloride in 100 ml of pyridine. The rate of addition was adjusted so that a reaction temperature of 40-45° was maintained without heating. After addition had been completed the dark solution was heated at 45° for 2 hr, then cooled and slowly poured into 1.5 liters of stirring 15% hydrochloric acid. The purple solid was filtered and washed with water.

Recrystallization from aqueous acetone gave 50.0 g (76%) of *N,N'*-di-*p*-toluenesulfonyl benzidine, m.p. 241-243° (reported m.p. 243°) (Ref. 41). The infrared spectrum is shown in Figure 80.

TABLE III

VISCOSIMETRIC DATA ON BBL POLYMER

BBL POLYMER - CELANESE CORPORATION LOT NO. 19273-34, 31 JANUARY 1972
BEFORE PURIFICATION

<u>Time^{a/}</u> <u>(sec)</u>	<u>Conc. C</u> <u>(g/dl)</u>	<u>Avg. T</u> <u>(sec)</u>	<u>η_r</u>	<u>η_{sp}</u>	<u>$\frac{\eta_{sp}}{C}$</u>	<u>$\frac{\ln \eta_r}{C}$</u>
78.3, 78.3, 78.3	0.0625	78.3	1.2177	0.2177	3.4832	3.182
92.1, 92.1, 92.1	0.125	92.1	1.4323	0.4323	3.4584	2.805
105.9, 105.8, 105.9	0.250	105.9	1.6465	0.6465	2.5860	2.003
169.7, 169.7, 169.8	0.500	169.7	2.6396	1.6396	3.2792	1.9416
64.3, 64.3, 64.3	Solvent ^{b/}	64.3	$[\eta]^c/$ = Indeterminate Value			

BBL POLYMER - CELANESE CORPORATION LOT NO. 19273-34, 31 JANUARY 1972
AFTER PURIFICATION

<u>Time^{a/}</u> <u>(sec)</u>	<u>Conc. C</u> <u>(g/dl)</u>	<u>Avg. T</u> <u>(sec)</u>	<u>η_r</u>	<u>η_{sp}</u>	<u>$\frac{\eta_{sp}}{C}$</u>	<u>$\frac{\ln \eta_r}{C}$</u>
73.1, 72.9, 72.9	0.100	73.0	1.1455	0.1455	1.4550	1.3583
87.5, 87.6, 87.5	0.250	87.5	1.3740	0.3740	1.4960	1.2725
105.2, 105.2, 105.3	0.400	105.2	1.6519	0.6519	1.6298	1.2548
117.0, 117.1, 117.1	0.500	117.1	1.8378	0.8378	1.6756	1.2171
64.3, 64.3, 64.3	Solvent ^{b/}	64.3	$[\eta]^c/$ = 1.38			

a/ Temperature = 30°

b/ Methanesulfonic acid

c/ Intrinsic viscosity, $[\eta]$, was obtained in the conventional manner by extrapolation of the intercept of the plots of the reduced specific viscosity, η_{sp}/C , and the inherent viscosity, $\ln \eta_r/C$, (see Figures 77 and 78).

Repetition of the procedure on a 0.54 mole scale gave 87.1 g (66%) of the product after two recrystallizations. The sample had a melting range of 242-244°.

A 30.0 g (0.061 mole) sample of N,N'-di-p-toluenesulfonyl benzidine was added portion-wise to 150 ml of stirring concentrated nitric acid which had been warmed to 40°. The rate of addition was adjusted so that the temperature was maintained at 40-45°. After addition had been completed (~ 30 min) the mixture was stirred without heating for 2 hr. The reaction mixture then was cooled to 15° and poured onto ice. The solid was filtered and slurry washed three times with water, once with ethanol, and finally with petroleum ether. After air drying, the sample was recrystallized from pyridine-ethanol. A total of 21.0 g (59%) of 3,3'-dinitro-N,N'-di-p-toluenesulfonyl benzidine was obtained, m.p. 227-229°, (reported m.p. 220°) (Ref. 40).

A second reaction was carried out on a 0.20 mole scale to afford 89.7 g (77%) of additional product, m.p. 227-229°.

b. Physical properties: 3,3'-Dinitro-N,N'-di-p-toluenesulfonyl benzidine was a dark yellow solid, m.p. 227-229°. The infrared spectrum is reported in Figure 81.

c. Purity: Elemental analysis indicated the sample was of 99+% purity.

Anal. Calcd. for $C_{26}H_{22}N_4O_8S_2$: C, 53.60, H, 3.81; N, 9.62. Found: C, 53.92; H, 3.66; N, 9.49.

28. 1,2-Dinitro-4-fluorobenzene

This compound was prepared in 55% yield by nitration of m-fluoronitrobenzene (Ref. 42).



a. Synthesis: To 260 ml of a 1:1 mixture of concentrated nitric acid to concentrated sulfuric acid at 50° was added 24.0 g (0.17 mole) of m-fluoronitrobenzene. Addition was made dropwise at a rate which allowed the reaction temperature to reach 58-60° during the addition period of ~ 1 hr. The reaction was stirred for an additional hour at 50°, then cooled and

poured on ice. The bright yellow solid was filtered and washed several times with water. The solid was then slurry washed three times with 10% sodium carbonate solution and twice with water. After these washings, the solid was very light yellow in color. Recrystallization from aqueous ethanol gave 20.5 g (65%) of 1,2-dinitro-4-fluorobenzene, m.p. 52-54° (reported m.p. 55-56°) (Ref. 42).

A second reaction was carried out on a 1.51 mole scale to afford 153.0 g (55%) of light yellow product, m.p. 52-54°.

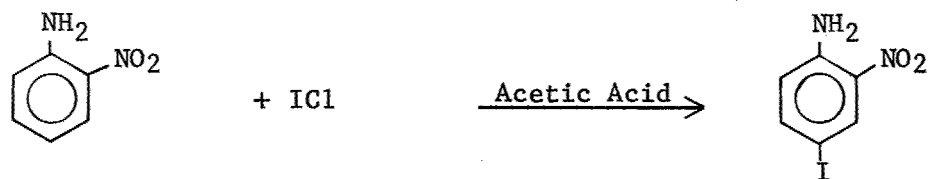
b. Physical properties: 1,2-Dinitro-4-fluorobenzene was a pale yellow solid, m.p. 52-54°. The infrared spectrum is shown in Figure 82.

c. Purity: Purity was assayed at 99+% by elemental analysis.

Anal. Calcd. for $C_6H_3N_2O_4F$: C, 38.72; H, 1.62; N, 15.06. Found: C, 38.46; H, 1.66; N, 14.72.

29. p-Iodo-o-nitroaniline

This compound was prepared in a 22% yield on treatment of o-nitroaniline with iodine monochloride (Ref. 1).



a. Synthesis: To a solution of 13.8 g (0.1 mole) of o-nitroaniline in 150 ml of glacial acetic acid was added 16.3 g (0.1 mole) of iodine monochloride (Alfa Ventron) over a period of 15-20 min. A slight exotherm to 30° was noted during the course of addition. After completion of addition, the solution was heated under reflux for 2.5 hr; then cooled to room temperature. The solution was diluted by dropwise addition of 250 ml of water. The dark brown precipitate was filtered and washed with water. The crude product was oven dried, and then recrystallized from ethanol to afford 5.5 g (21%) of p-iodo-o-nitroaniline m.p. 123-125° (reported m.p. 124-125°) (Ref. 1).

A second reaction was carried out on a 1.07 mole scale. The iodine monochloride used in this reaction, however, was of questionable purity. The reagent as received from Alfa was a mixture of liquid and solid. The liquid portion was decanted and added dropwise. The solid was dissolved in

acetic acid and added as a solution. On work-up, water addition gave only heavy tar instead of a filterable solid. The tar was stirred with warm ethanol in an attempt to crystallize the material. On examination of the ethanol mixture, three distinct layers were found to be present. The middle layer was ethanol-water. The top layer slowly crystallized to give an unidentified product. An infrared spectrum of this material indicated the solid was neither *o*-nitroaniline nor desired product. The bottom layer crystallized from benzene-petroleum ether (b.p. 60-90°) to afford 44 g of crude product, m.p. 70-100°. Recrystallization from chloroform gave 22.5 g (8%) of product, m.p. 123-126°.

A second large scale reaction (1.53 mole) was carried out with iodine monochloride obtained from Fisher Chemical Company. As received from the supplier this material was also a liquid-solid mixture. However, slight warming of the container with warm water melted the solid phase. The iodine monochloride was then added dropwise, and the reaction was carried out as before. A heavy oil was again thrown out of solution on dilution. The mixture was allowed to stand for several days, then the aqueous phase was decanted from the residue which had partially solidified. The mass was stirred with 1.5 liter of cold benzene, and the resultant rust-colored solid was filtered. On recrystallization from chloroform a total of 88.1 g (23%) of *p*-iodo-*o*-nitroaniline was obtained, m.p. 123-126°.

The two samples obtained from the large-scale reactions were combined and recrystallized again from chloroform to afford 87.0 g of brown product, m.p. 125.5-127°.

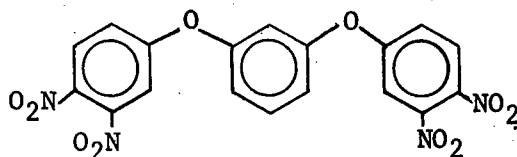
b. Physical properties: *p*-Iodo-*o*-nitroaniline was a brown solid, m.p. 125.5-127°. The infrared spectrum is reported as Figure 83.

c. Purity: The sample purity was assayed at 99+% by elemental analysis.

Anal. Calcd. for $C_6H_5N_2O_2I$: C, 27.29; H, 1.91; N, 10.61. Found: C, 27.03; H, 1.66; N, 10.45.

30. 1,3-Bis(3,4-dinitrophenoxy)benzene

This compound was synthesized by a proprietary procedure, (Ref. 1). The chemical structure of the compound is given below.



a. Purification: Approximately 40 g of crude product was dissolved in benzene and stirred with 50 g of silica gel (Fisher Scientific Company, 28-200 mesh/Grade 12). The benzene was evaporated in vacuo and the powder was loaded on a silica gel column (400 g) which had been slurry packed with 75% benzene-25% hexane solution. Initial elution with 8 liters of 3:1 benzene:hexane mixture gave 11 g of starting material. Continued elution with a 9:1 benzene:hexane solution gave 2.0 g of a mixture of which the major component was an unidentified by-product. Trace amounts of product were eluted also. The desired product was obtained as an oil on elution with 2 liters of 85% benzene-15% ethyl acetate. It was necessary to elute the product at a slow rate because of the heat developed as the yellow product band moved down the column. The oil was then dissolved in 700-800 ml of refluxing anhydrous ethanol. On slow cooling, 14 g of yellow solid product precipitated.

This material was combined with an additional 27 g obtained from two repetitions of the chromatography procedure. The combined solids were dissolved in 1,800 ml of boiling anhydrous ethanol and the solution was allowed to slowly cool to room temperature. (Recrystallization was difficult to effect because of the tendency for the product to oil.) A first crop of 19 g was obtained with an additional 12.5 g of product obtained in four crops on concentration of the mother liquors. Because of the differences in appearance and melting characteristics, thin-layer chromatography was carried out on samples from each fraction. The chromatography was performed on Eastman Chromatogram Sheet No. 6060, silica gel with fluorescent indicator. The solvent was benzene. The results are tabulated below, along with melting points and fraction weights.

Fraction		m.p.	Starting	Unknown	Product
No.	Wt (g)		Material (R_f 0.95)	By-Product (R_f 0.76)	
1	19.0	105-111°	-	Trace	Major
2	5.0	107-110°	-	Trace	Major
3	3.0	104-110°	-	-	Major
4	2.5	107.5-110.5°	-	-	Major
5	2.0	< 90°	-	Major	Major

Because Fraction 5 contained a large amount of the unknown component, it was discarded. The other fractions were combined as one sample. The discrepancy in melting points for the four fractions was felt to be an artifact of the crystallization process and not indicative of sample purity.

b. Physical properties: 1,3-Bis(3,4-dinitrophenoxy)benzene was a yellow solid, m.p. 107.5-110.5° (reported m.p. 106-108.5°) (Ref. 1). The infrared spectrum is shown in Figure 84.

c. Purity: The sample was of 99% purity based on thin-layer chromatography and elemental analysis.

Anal. Calcd. for $C_{18}H_{10}N_4O_{10}$: C, 48.88; H, 2.28; N, 12.67. Found: C, 48.99; H, 2.47; N, 12.19.

SECTION III

SUMMATION OF SAMPLE SHIPMENTS

Samples of compounds which were shipped during this report period are listed as follows:

<u>Compound</u>	<u>Purity (%)</u>	<u>Weight (g)</u>
Perfluoro- <u>n</u> -octyl iodide (Sample 1)	95-97.5	180.5
(Sample 2)	98.5	59.0
(Sample 3)	98.6	188.3
(Sample 4)	98.6	650.4
1,3-Bis(3-nitrophenoxy)benzene	99.0	10.0
1,3-Bis(3-aminophenoxy)benzene	99.0+	7.8
1'-Methyl-3'-keto-2,3-cyclopentenoace- naphthene (Sample 1)	99.0+	93.0
(Sample 2)	99.0	180.0
(Sample 3)	99.0	93.0
1'-Methyl-2,3-cyclopentenoacenaphthene	98.0	7.5
Pyracen-1,2-dione	95.0+	20.0
2,3,5,6-Tetrafluorothiophenol	99.0+	250.0
β -(3-Acenaphthoyl)propionic acid	99.0+	106.5
3,6-Dioxaoctanedioic acid	99.0+	167.0
4,8-Dioxaundecanedioic acid	99.0	210.0
1,8-Divinyl-naphthalene (Sample 1)	99.0+	100.0
(Sample 2)	99.0+	500.0
Bis-5,5'-acenaphthenyl(1,3-phenyl)ketone	99.0	42.0
5-Methyl-4,7-dioxadecanedioic acid	99.0	138.0
4,5-Dinitro-N,N'- <u>o</u> -phenylenebis(p-toluene- sulfonamide) (Sample 1)	99.0+	250.0
(Sample 2)	99.0+	256.0

<u>Compound</u>	<u>Purity (%)</u>	<u>Weight (g)</u>
2,3,5,6-Tetrafluorobenzene-1,4-dithiol	99.0+	112.0
Perfluoro- <u>n</u> -decyl iodide (Sample 1)	98.8	579.5
(Sample 2)	97.9	36.1
(Sample 3)	82.8	89.7
1,3-Diiodohexafluoropropane (Sample 1)	99.0+	105.0
(Sample 2)	99.0	202.0
4-Iodophenyl Acetate (Sample 1)	99.0+	100.0
(Sample 2)	99.0+	502.0
1,3-Bis(3-nitro-4-hydroxyphenyl)hexafluoropropane	99.0	25.9
4,8-Dibromo-1,5-bis(<u>p</u> -toluenesulfonamido)-naphthalene	99.0	96.4
1,3-Bis(4-hydroxyphenyl)hexafluoropropane	99.9	25.0
2,2'-Diiodobenzidine (Sample 1)	99.0	58.5
(Sample 2)	99.0	80.0
<u>o</u> -Divinylbenzene (Sample 1)	96.0	9.3
(Sample 2)	98.0	159.0
BBL Polymer (Sample 1)	Purified	2.0
(Sample 2)	Unpurified	2.5
3,3'-Dinitro-N,N'-di- <u>p</u> -toluenesulfonyl Benzidine	99.0	110.7
1,2-Dinitro-4-fluorobenzene	99.0+	75.0
<u>p</u> -Iodo- <u>o</u> -nitroaniline	99.0+	92.0
1,3-Bis(3,4-dinitrophenoxy)benzene	99.0	29.5

SECTION IV

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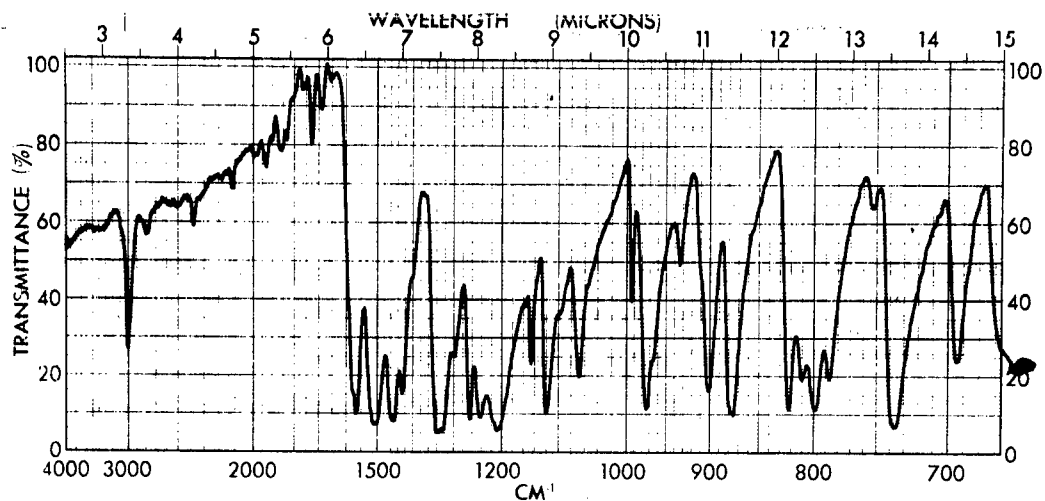


Figure 1 - Infrared Spectrum of 1,3-Bis(3-nitrophenoxy)-benzene (KBr)

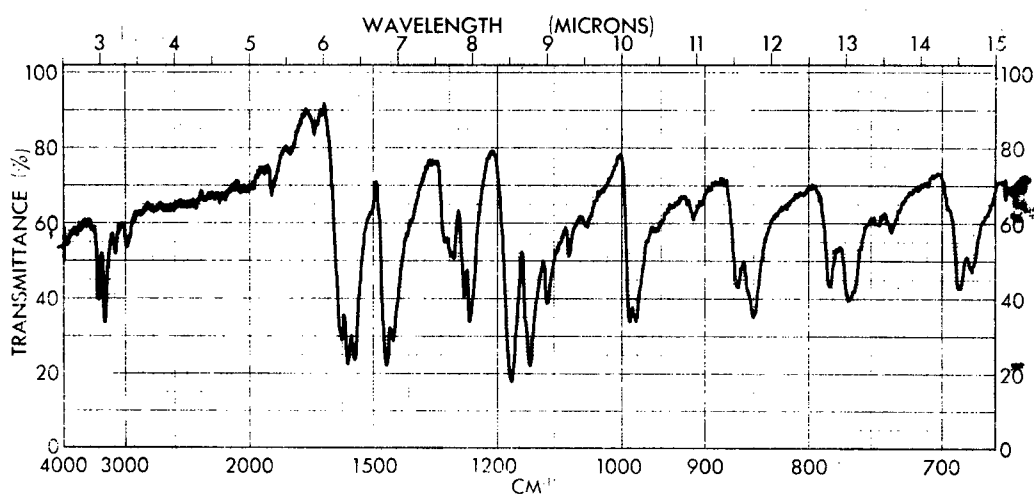


Figure 2 - Infrared Spectrum of 1,3-Bis(3-aminophenoxy)-benzene (KBr)

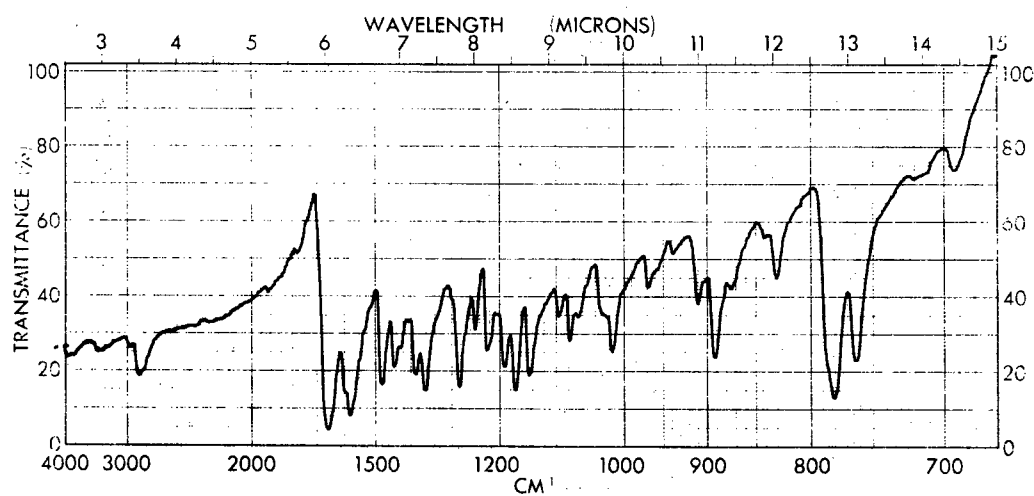


Figure 3 - Infrared Spectrum of 1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene (KBr)

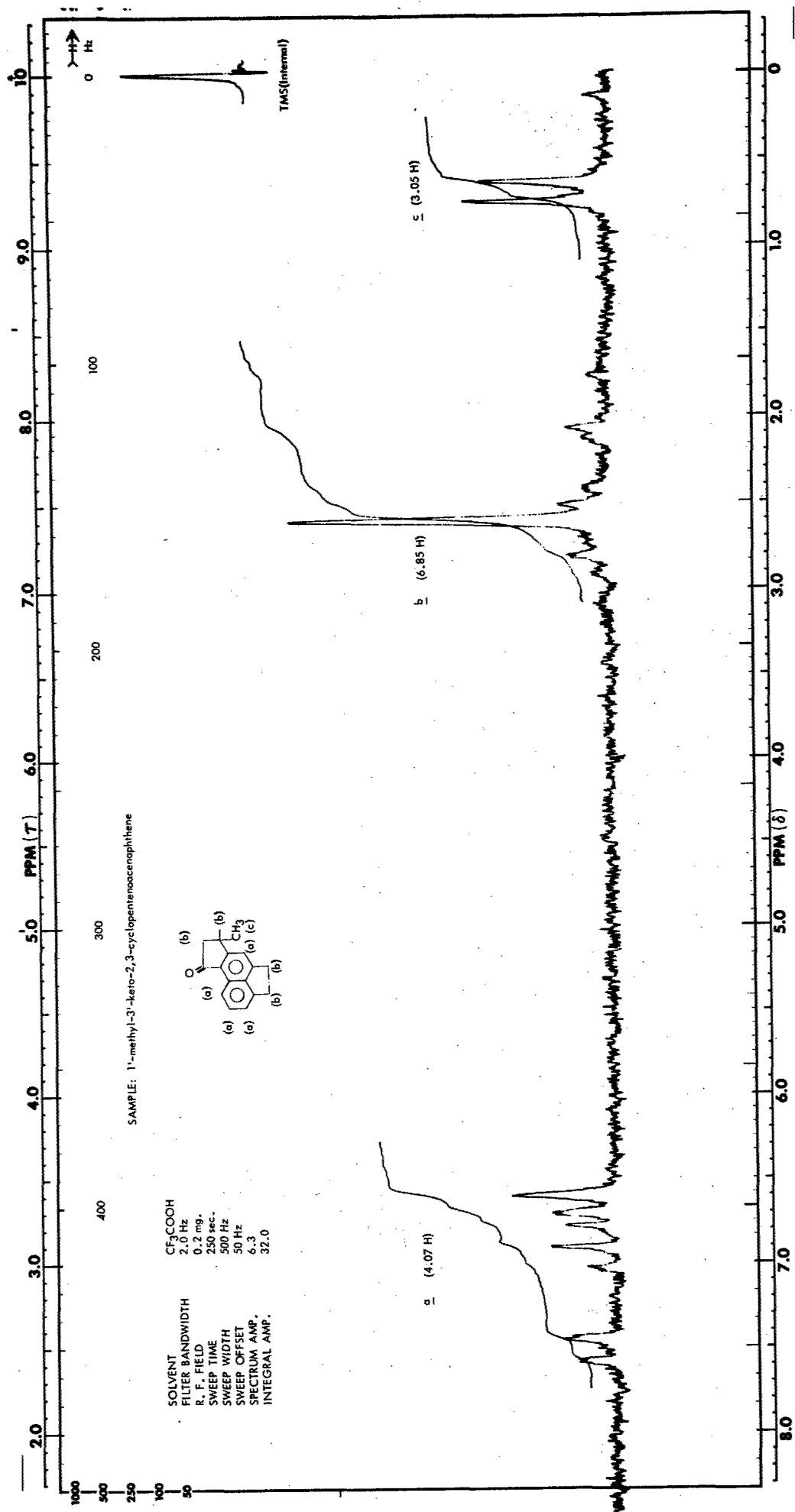


Figure 4 - NMR Spectrum of 1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene

1'-methyl-3'-keto-2,3-cyclopentenoacenaphthene
71-41-5
225°C, H₂ Flame
2 m., 5 % SF-96 on Gas Chrom Q
He Carrier--15 psig

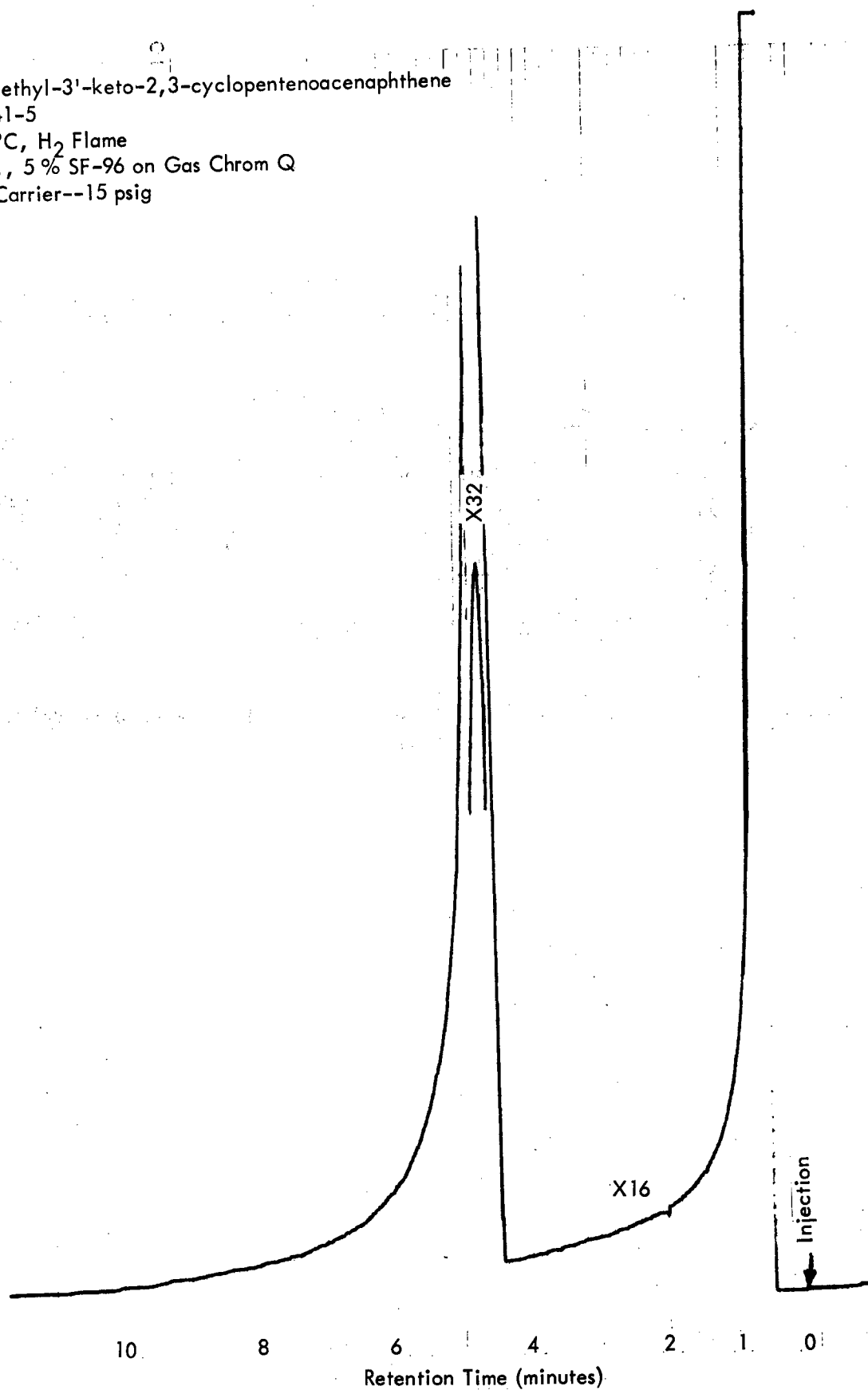


Figure 5 - Gas-Liquid Chromatogram of 1'-Methyl-3'-keto-2,3-cyclopentenoacenaphthene

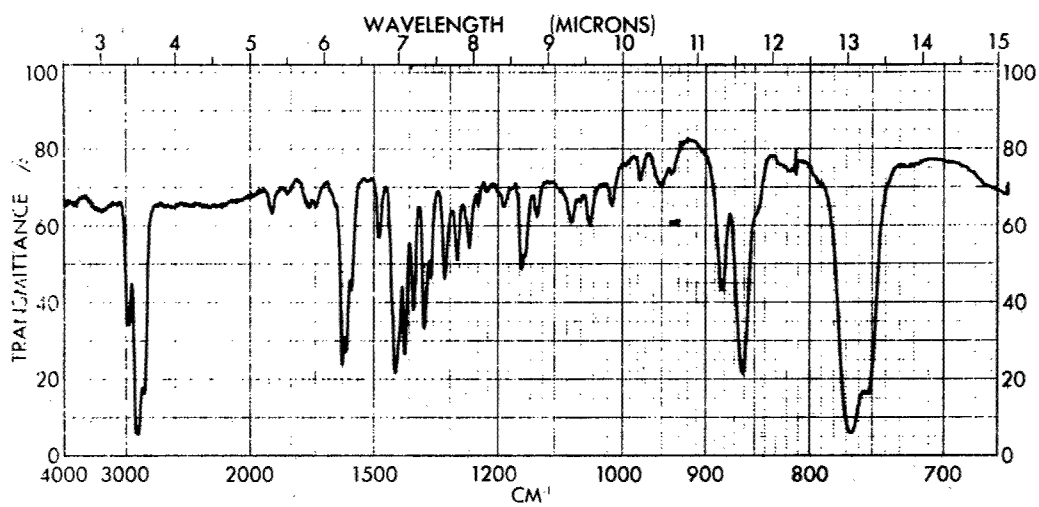


Figure 6 - Infrared Spectrum of 1'-Methyl-2,3-cyclopentenoacenaphthene (Liquid)

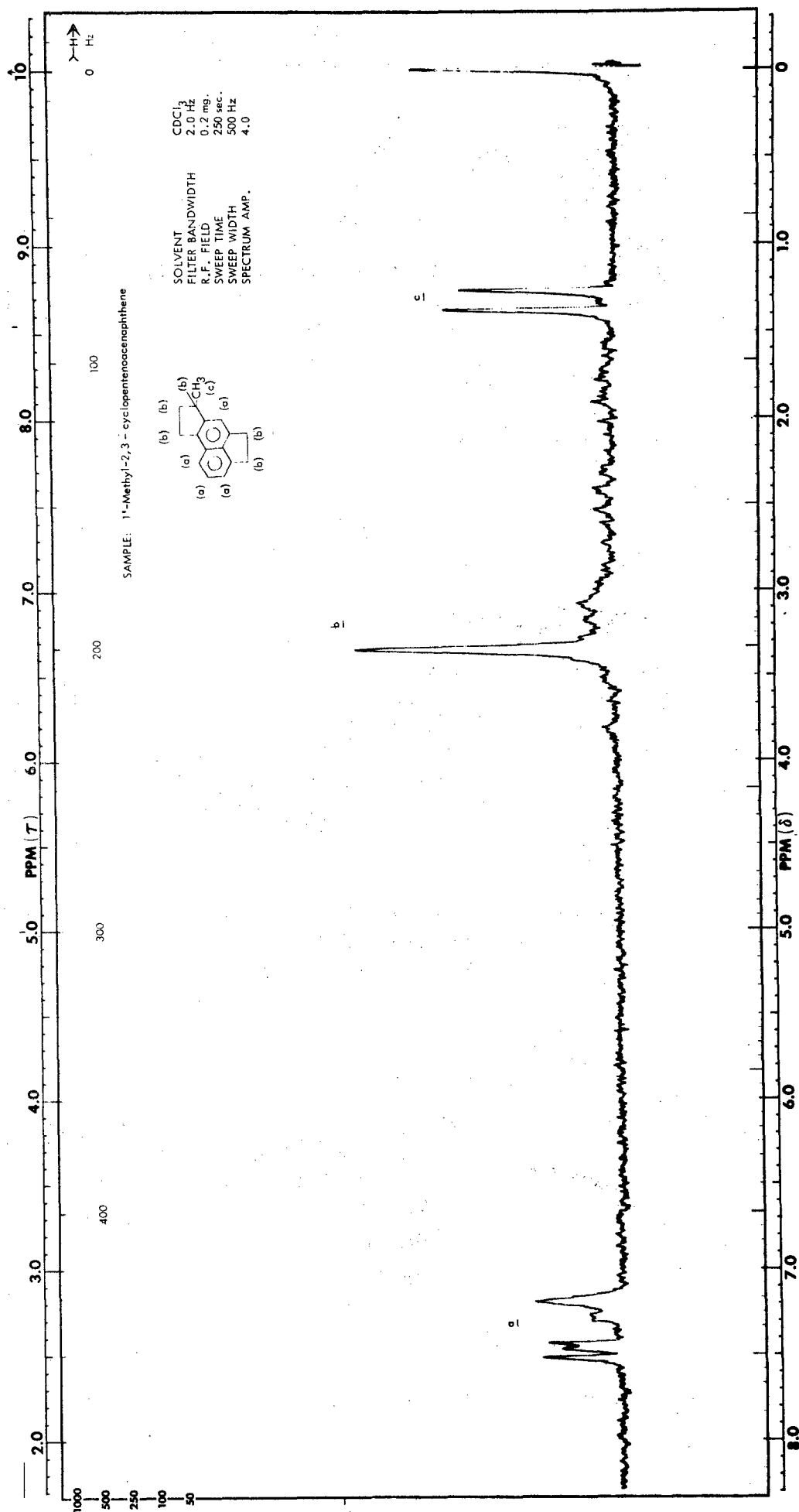


Figure 7 - NMR Spectrum of 1'-Methyl-2,3-cyclopentenoacenaphthene

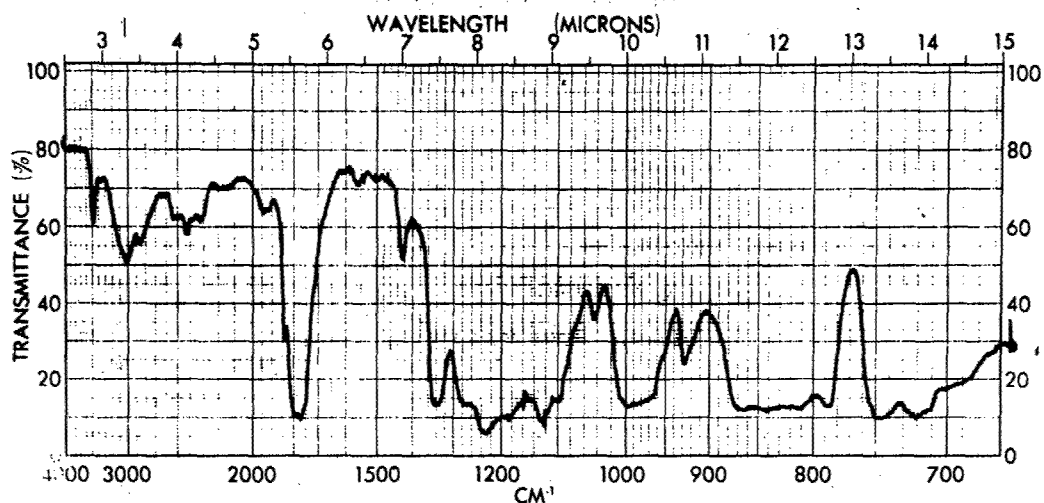


Figure 8 - Infrared Spectrum of Heptafluorobutyryl Chloride (Liquid)

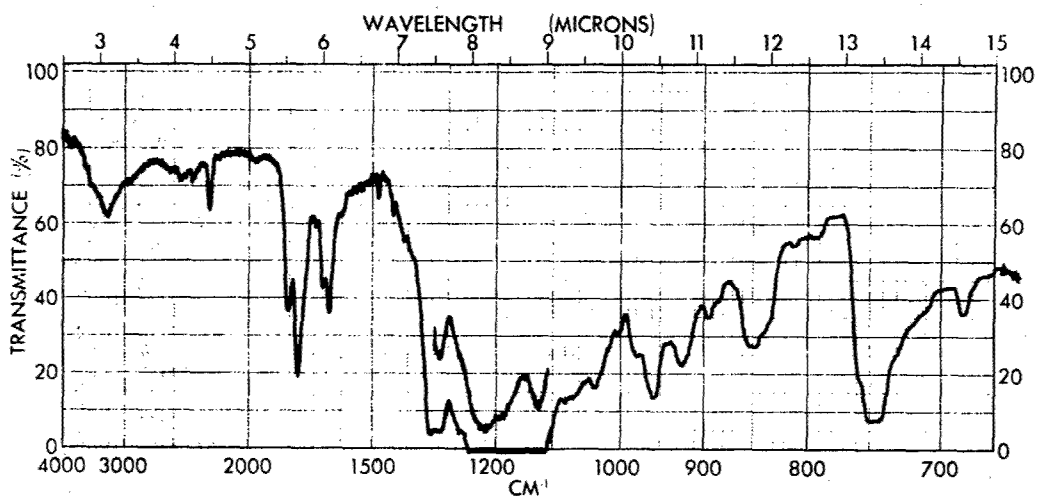


Figure 9 - Infrared Spectrum of Liquid Product Isolated from the Reaction of Perfluorobutyryl Chloride with Nickel Carbonyl (Liquid)

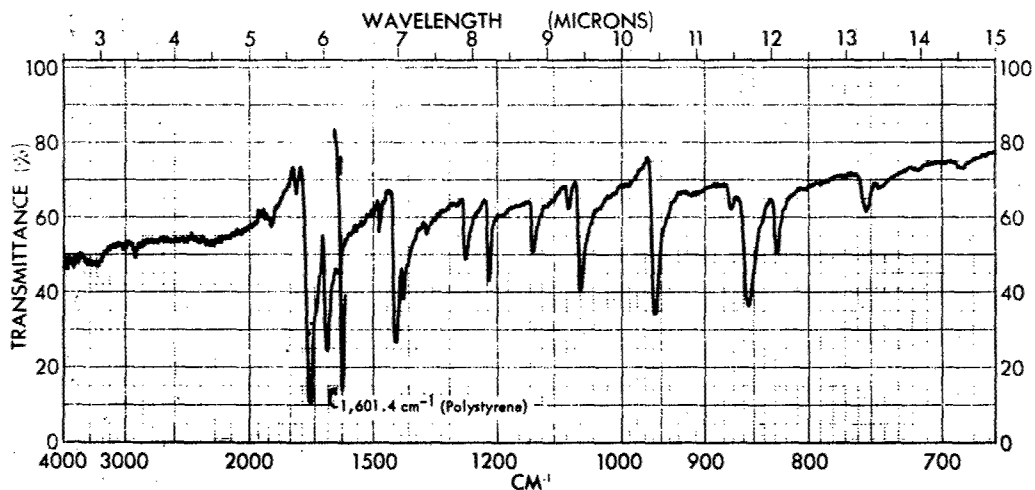


Figure 10 - Infrared Spectrum of Pyracen-1,2-dione (KBr)

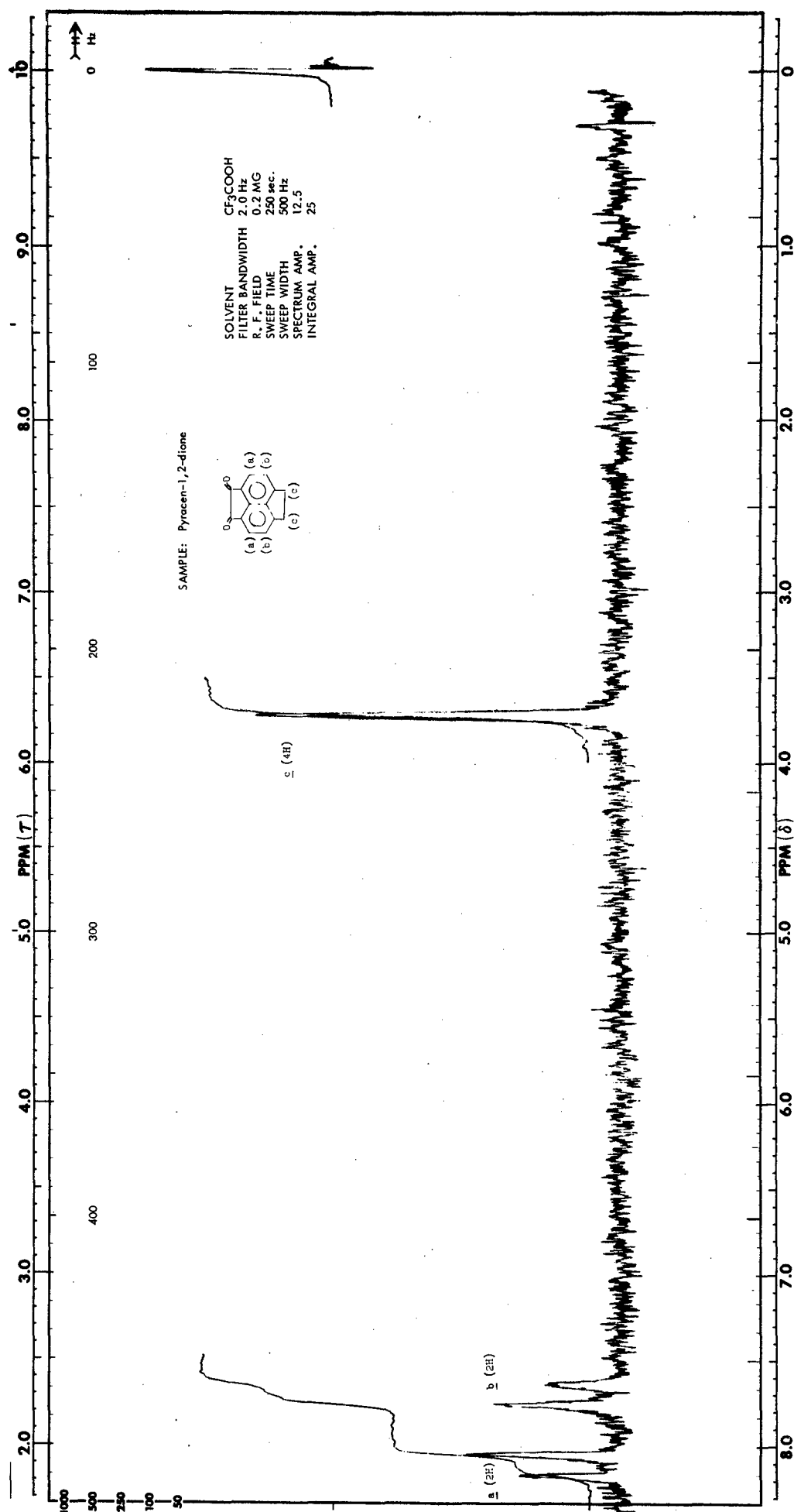


Figure 11 - NMR Spectrum of Pyracen-1,2-dione

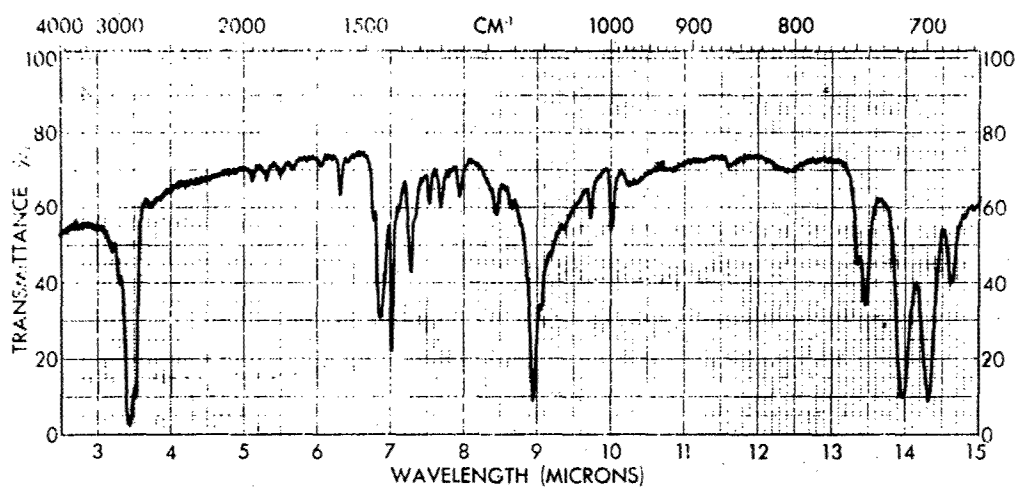


Figure 12 - Infrared Spectrum of Triphenylsilylamine (Nujol)

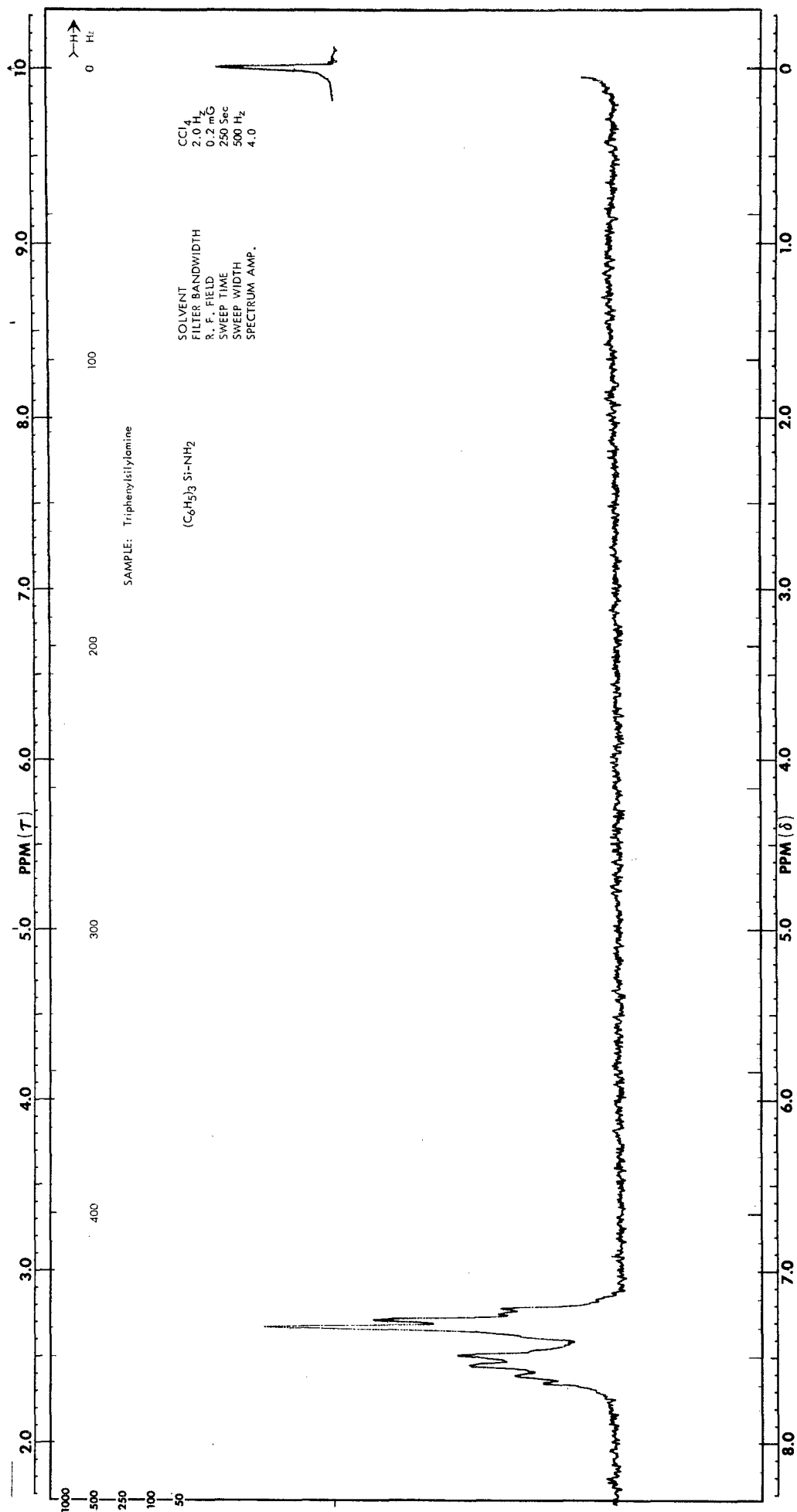


Figure 13 - NMR Spectrum of Triphenylsilylamine

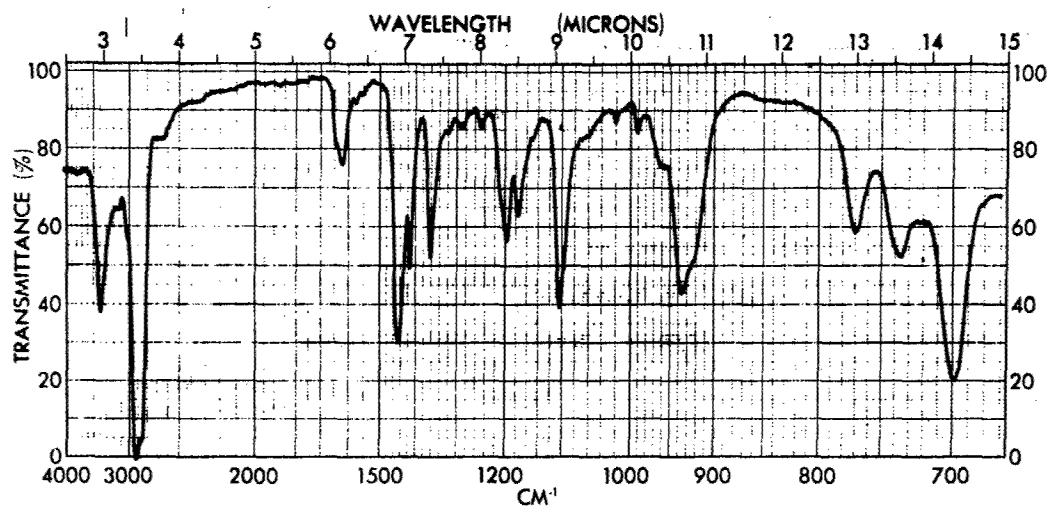


Figure 14 - Infrared Spectrum of Insoluble Product from the Attempted Preparation of 1,1,1-Trichloro-3,3,3-triphenyldisilazane (Nujol)

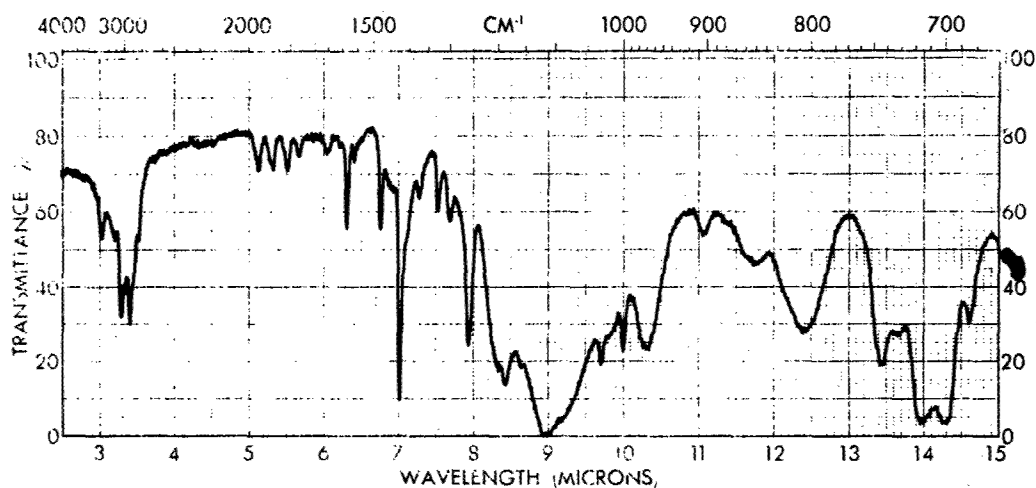


Figure 15 - Infrared Spectrum of Crude Product from the Attempted Preparation of 1,1,1-Trichloro-3,3,3-triphenyldisilazane (Liquid)

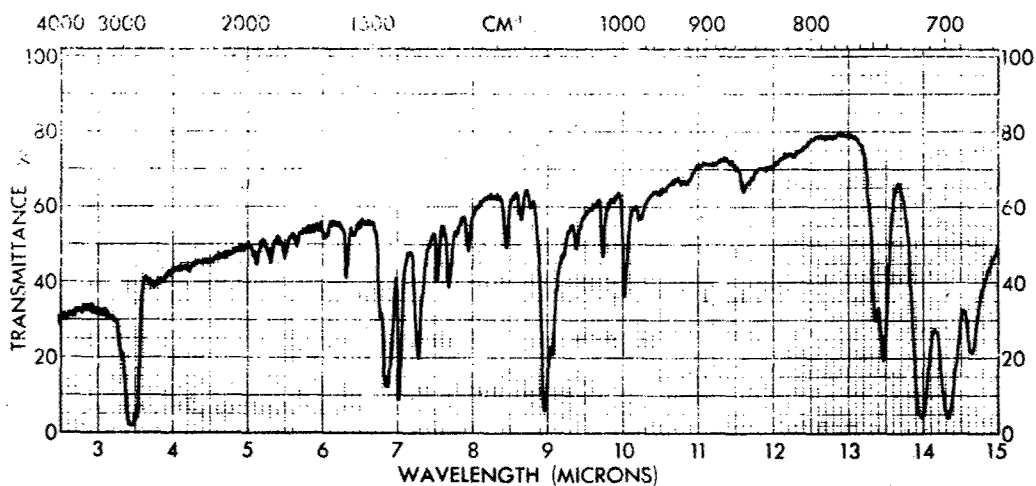


Figure 16 - Infrared Spectrum of Distilled Product from the Attempted Preparation of 1,1,1-Trichloro-3,3,3-triphenyldisilazane (Nujol) [Identical to $(C_6H_5)_3SiCl$]

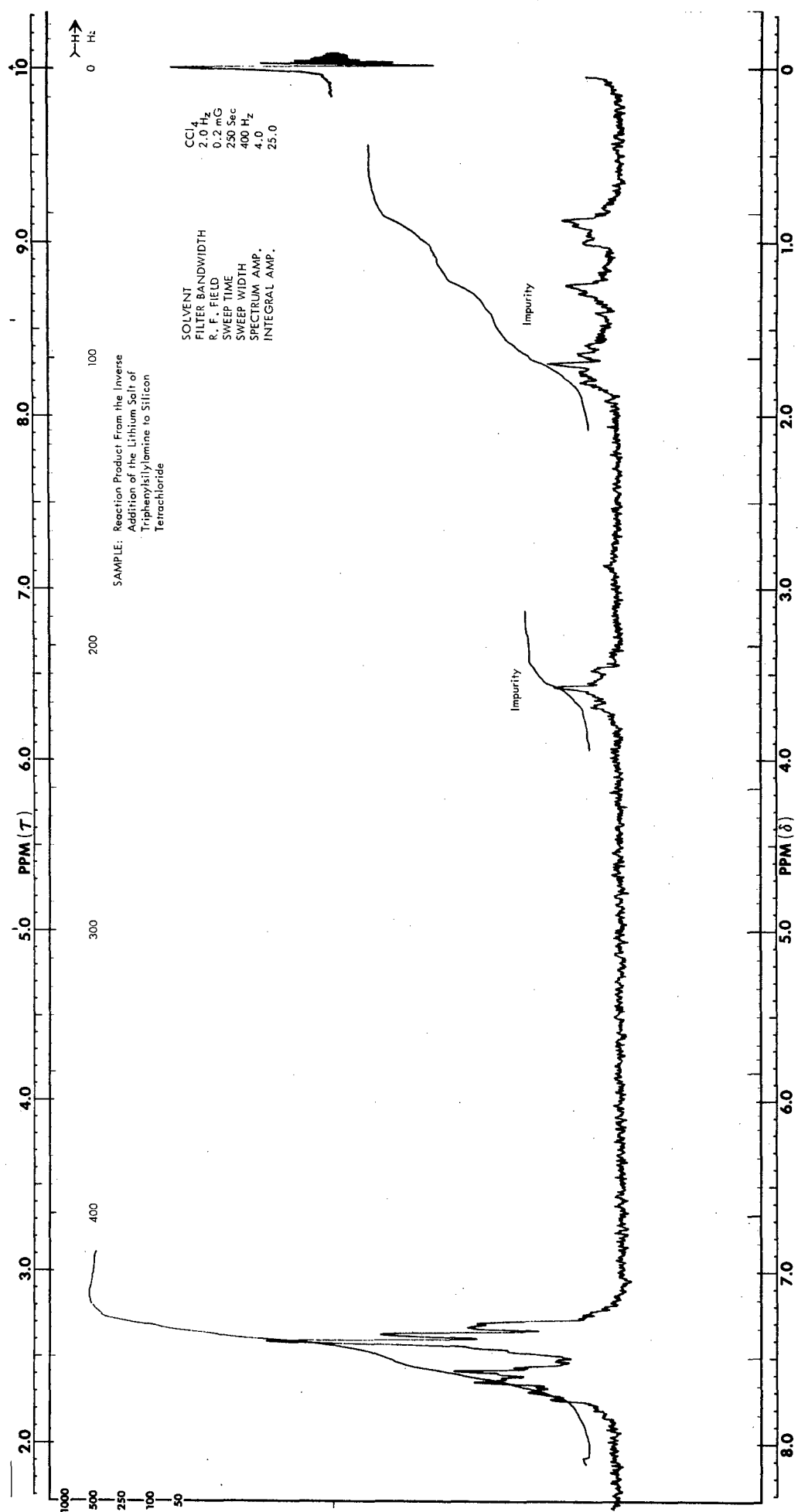


Figure 17 - NMR Spectrum of Crude Product from the Inverse Addition of the
 Lithium Salt of Triphenylsilylamine to Silicon Tetrachloride

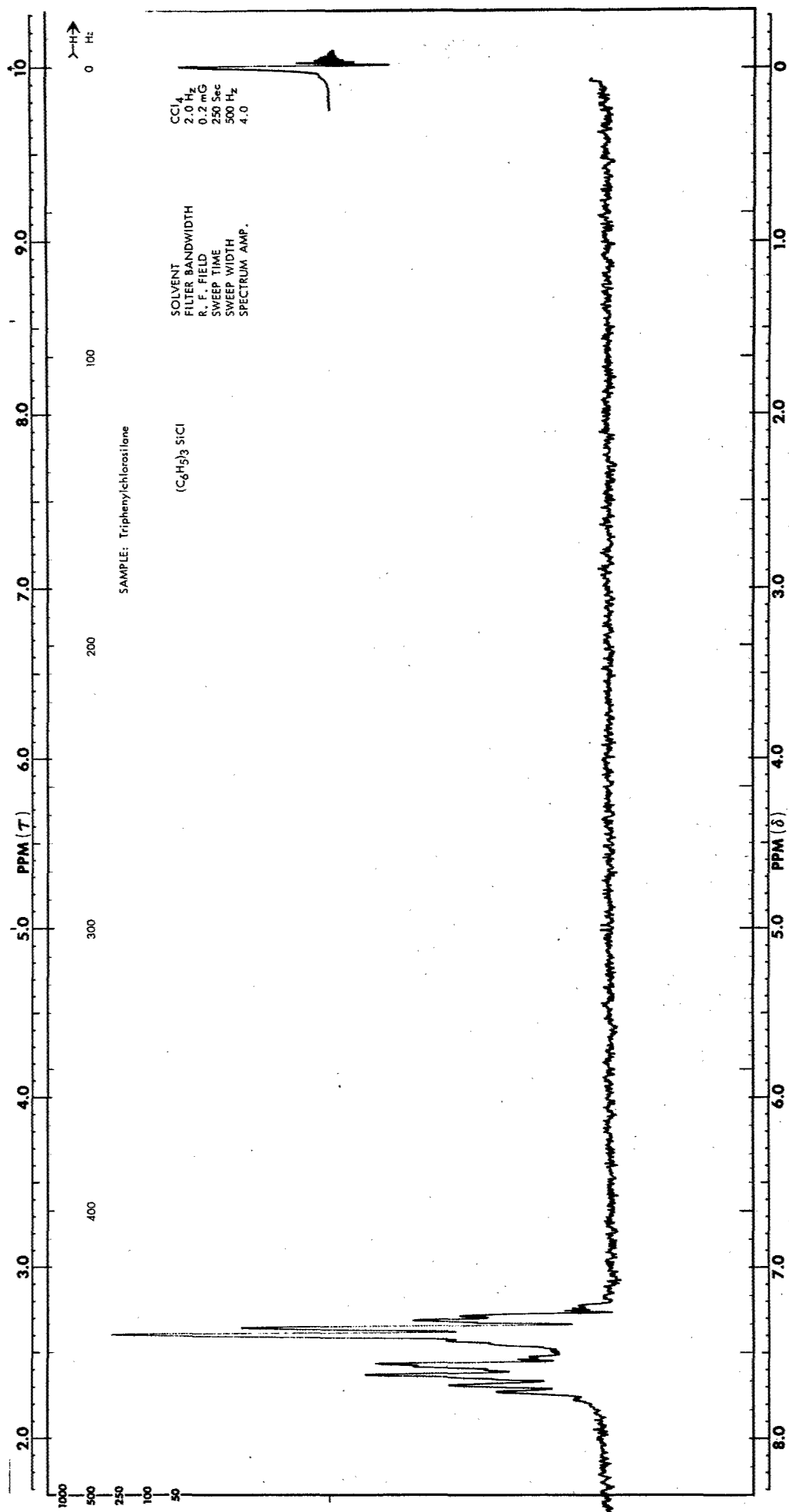
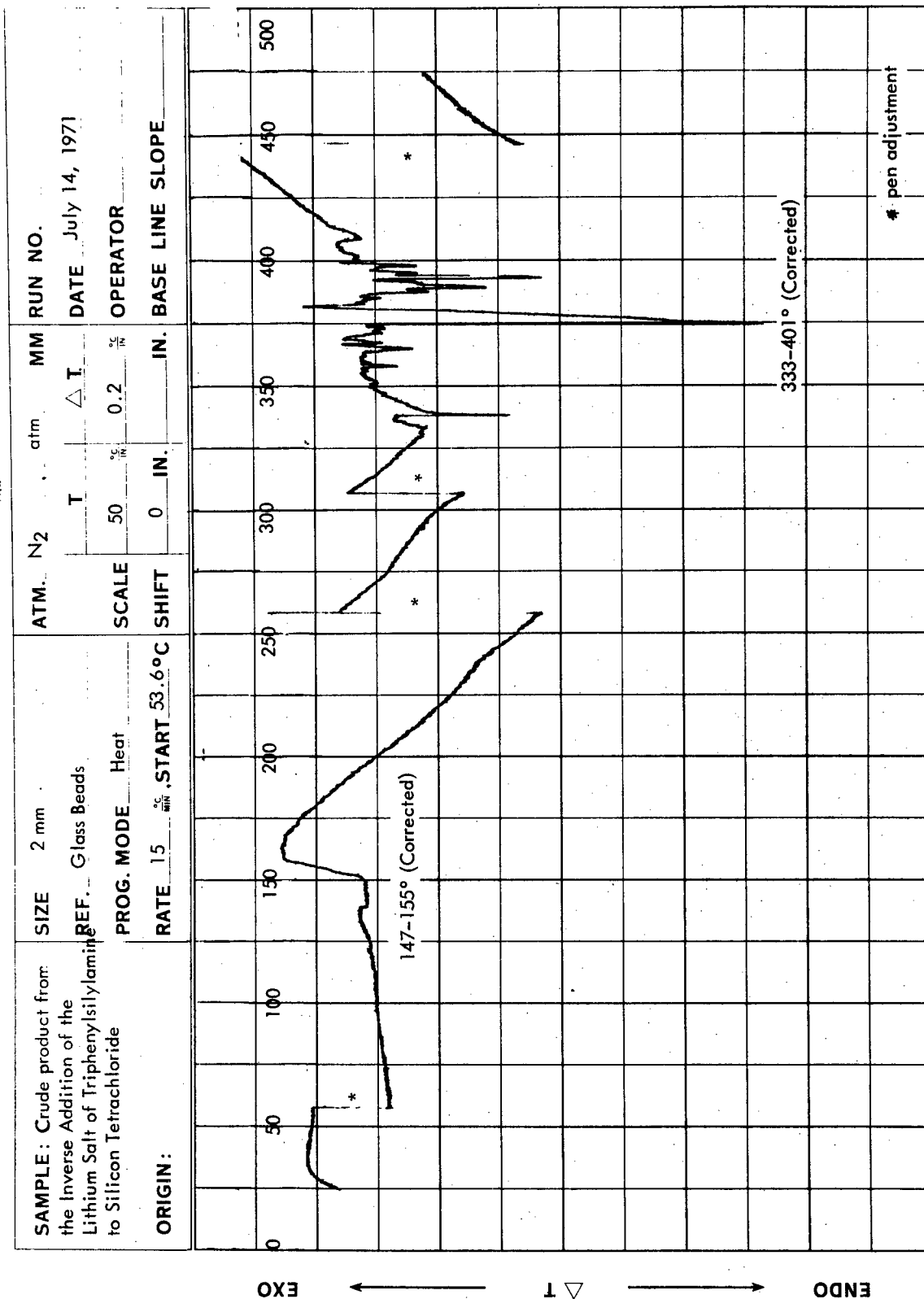


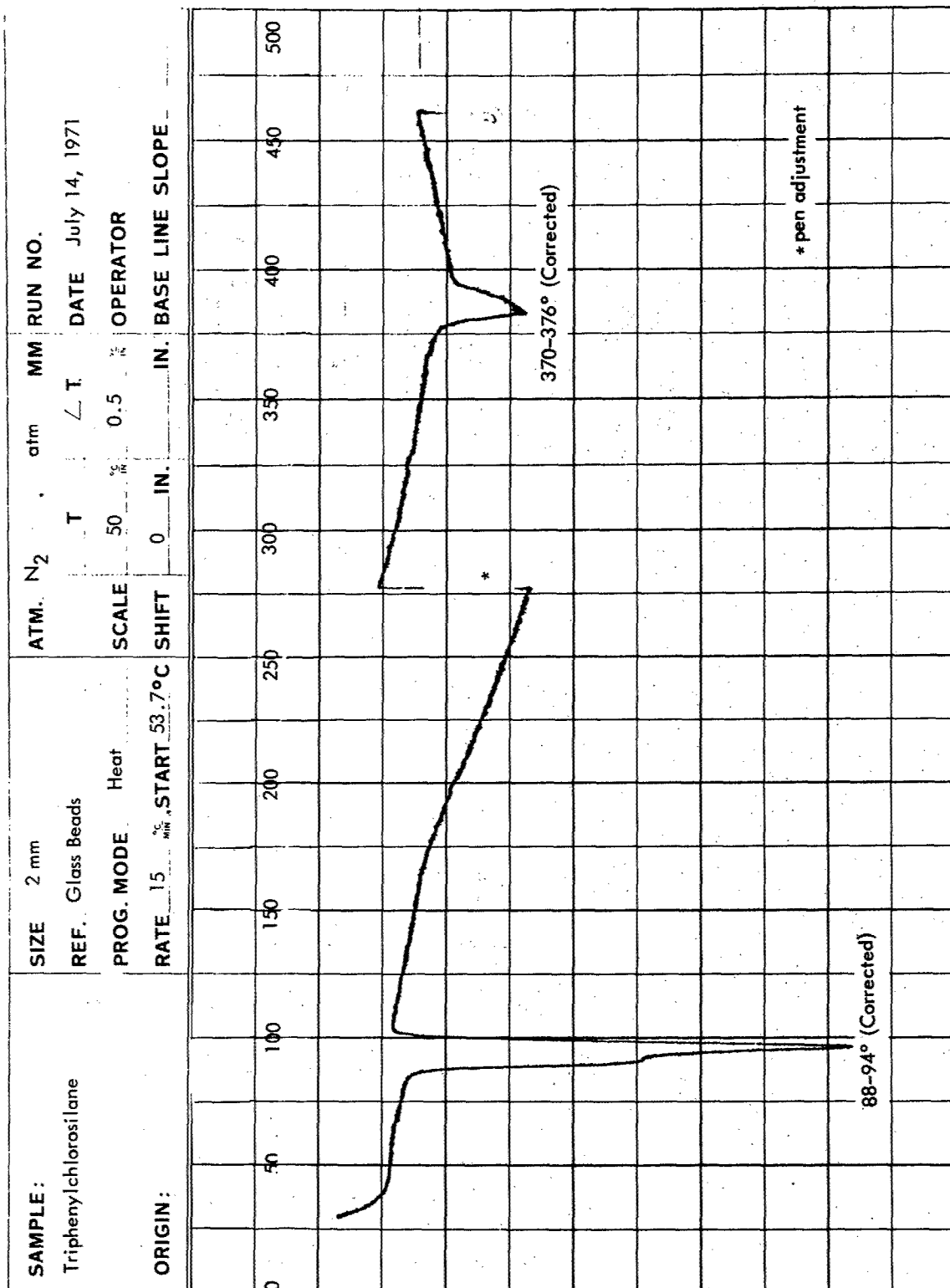
Figure 18 - NMR Spectrum of Triphenylchlorosilane



T, $^{\circ}\text{C}$ (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 19 - DTA of Crude Product from the Inverse Addition of the Lithium Salt of Triphenylsilylamine to Silicon Tetrachloride



T. °C (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 20 - DTA of Triphenylchlorosilane

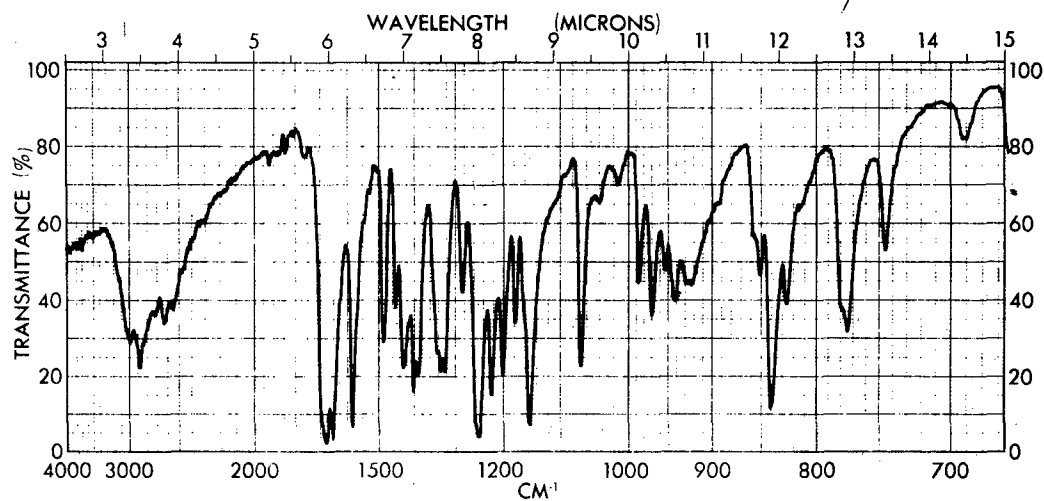


Figure 21 - Infrared Spectrum of β -(3-Acenaphthoyl)-propionic Acid (KBr)

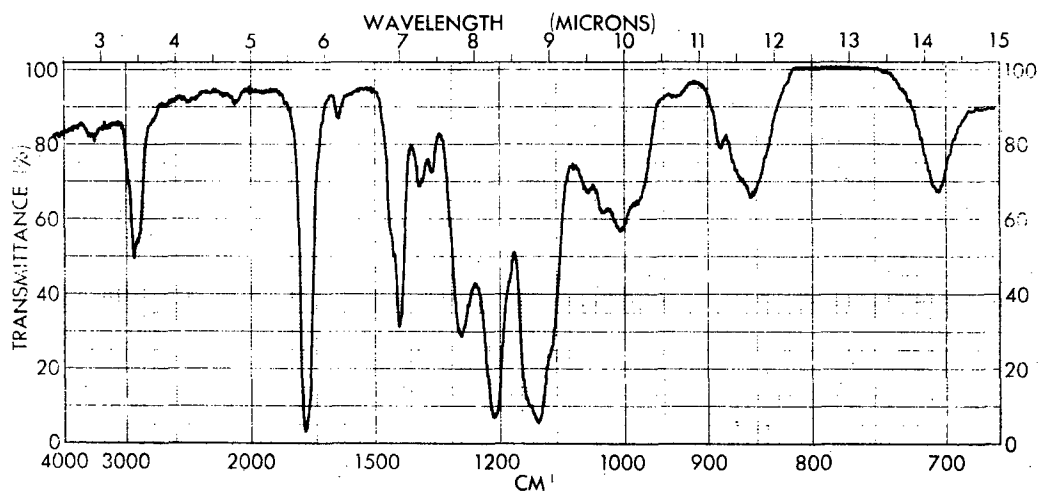
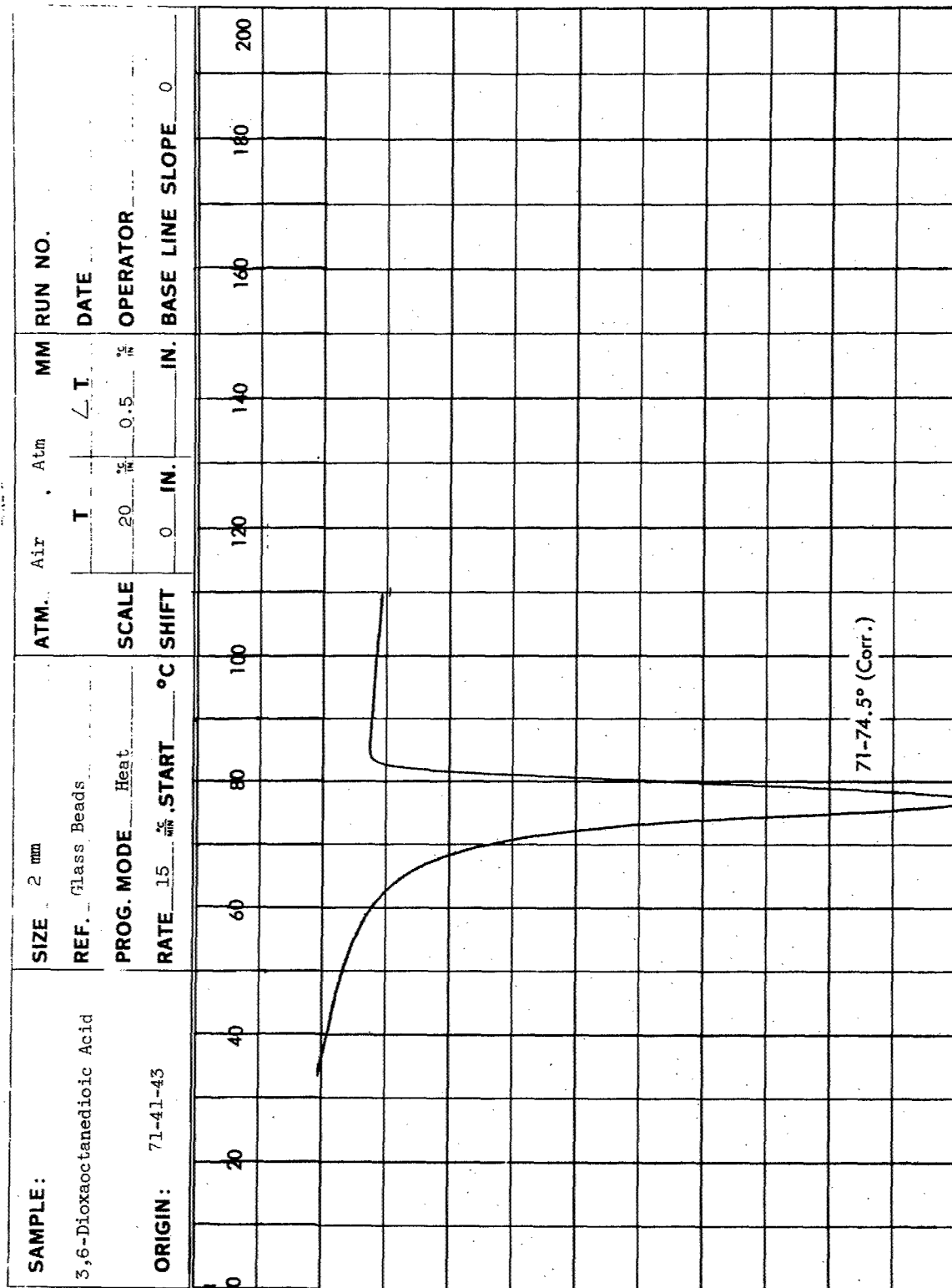


Figure 22 - Infrared Spectrum of Dimethyl-3,6-dioxatenedioate (Liquid)

SAMPLE:

RUN NO.:



T. $^\circ\text{C}$ (CHROMEL: ALUMEL)*

Figure 23 - DTA of 3,6-Dioxaoctanedioic Acid

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

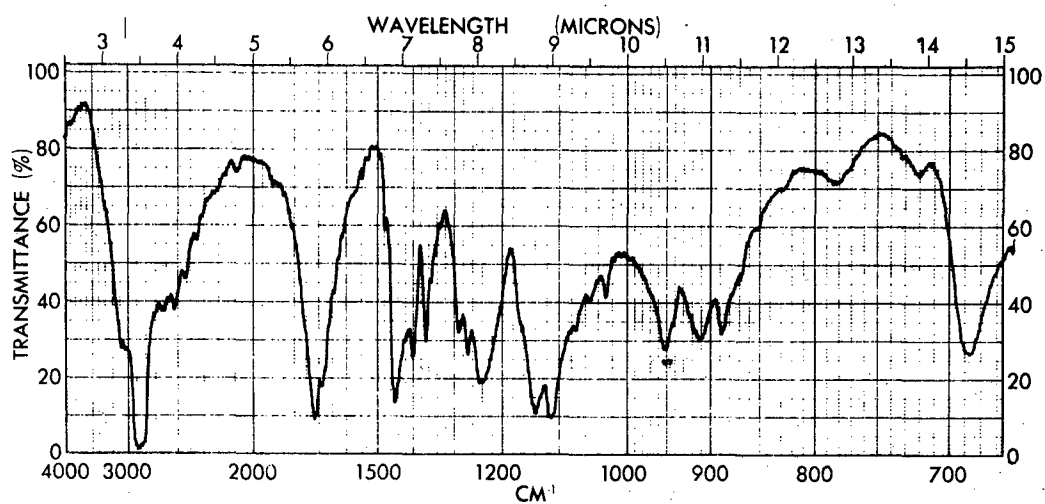


Figure 24 - Infrared Spectrum of 3,6-Dioxaoctanedioic Acid (Nujol)

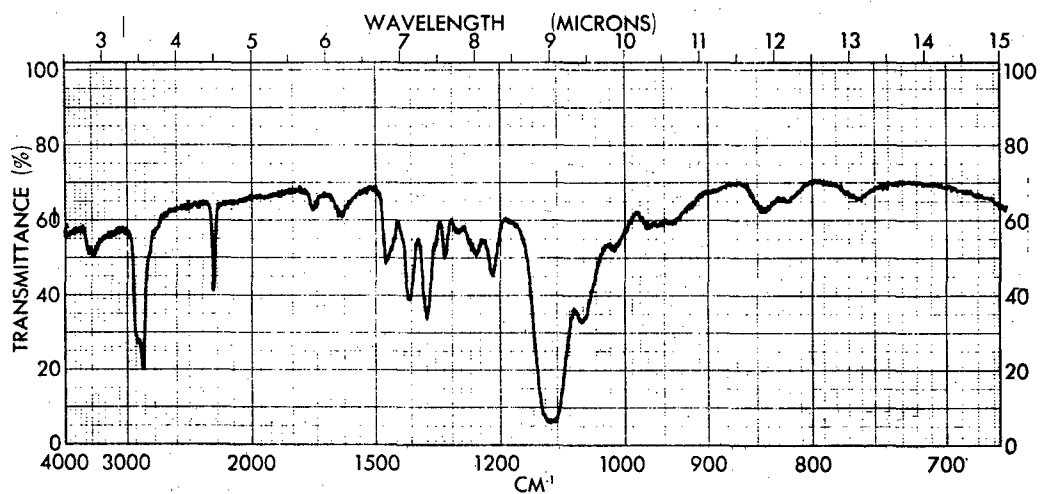
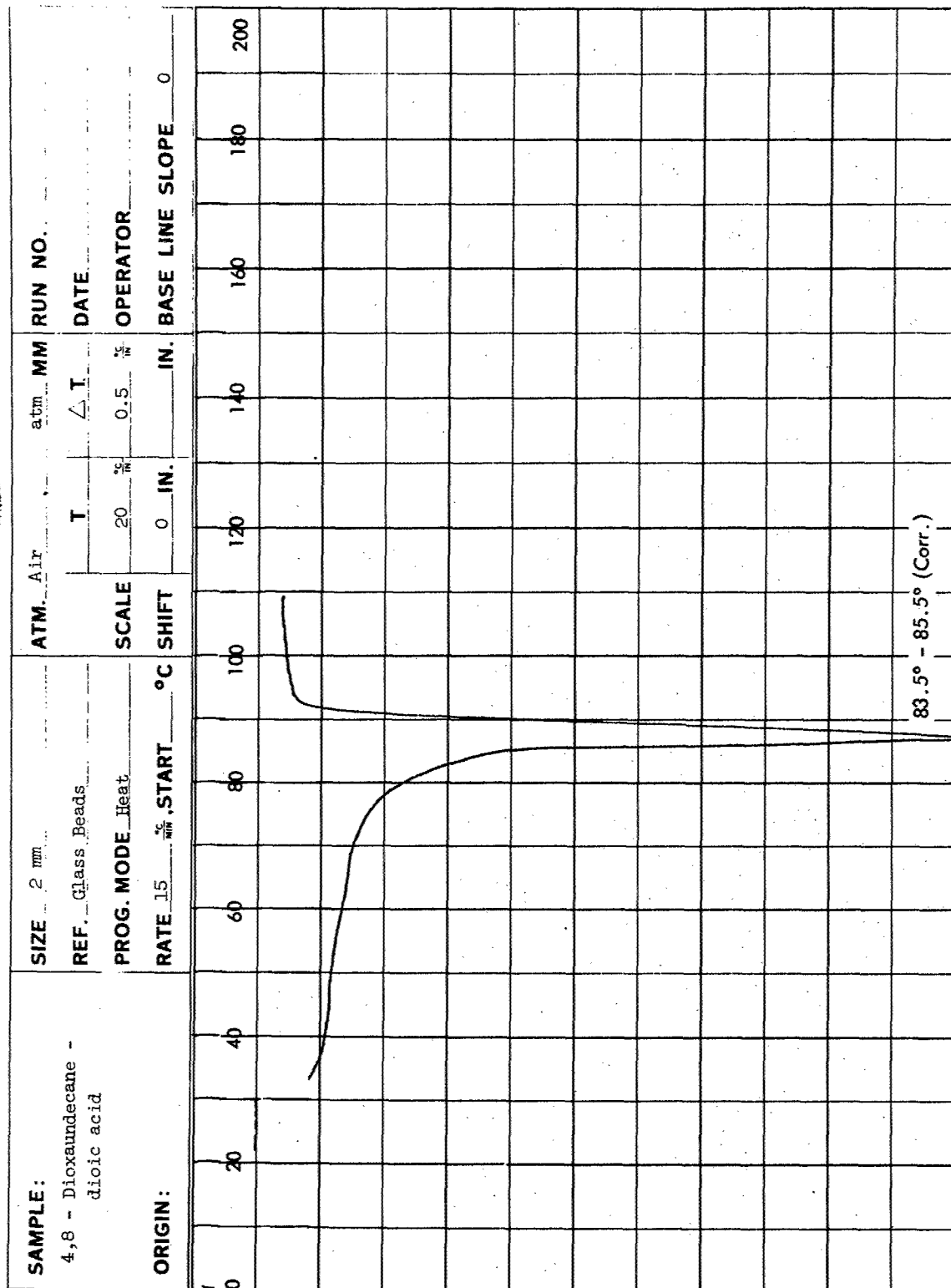


Figure 25 - Infrared Spectrum of 1,3-Di-(2-cyanoethoxy)propane (Liquid)



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 26 - DTA of 4,8-Dioxundecanedioic Acid

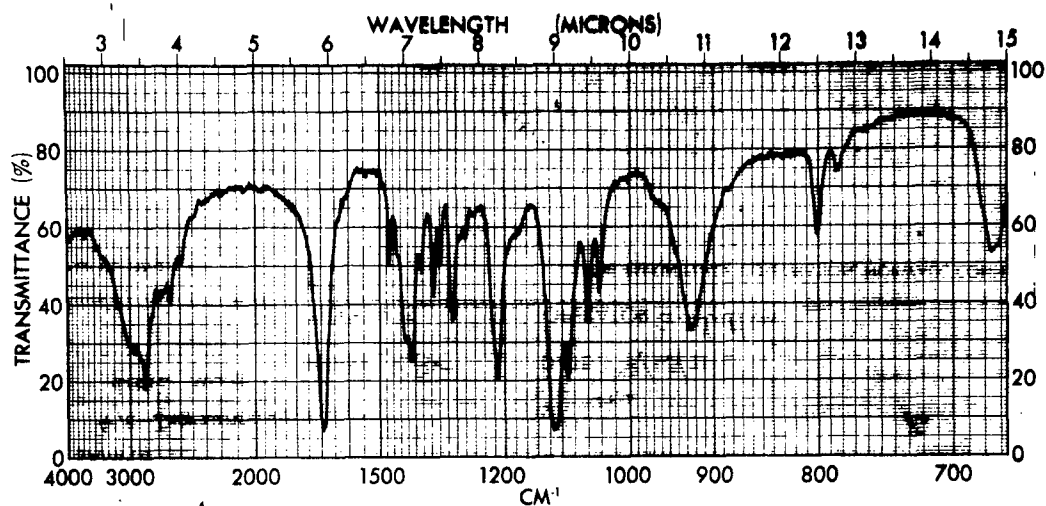


Figure 27 - Infrared Spectrum of 4,8-Dioxaundecanedioic Acid (KBr)

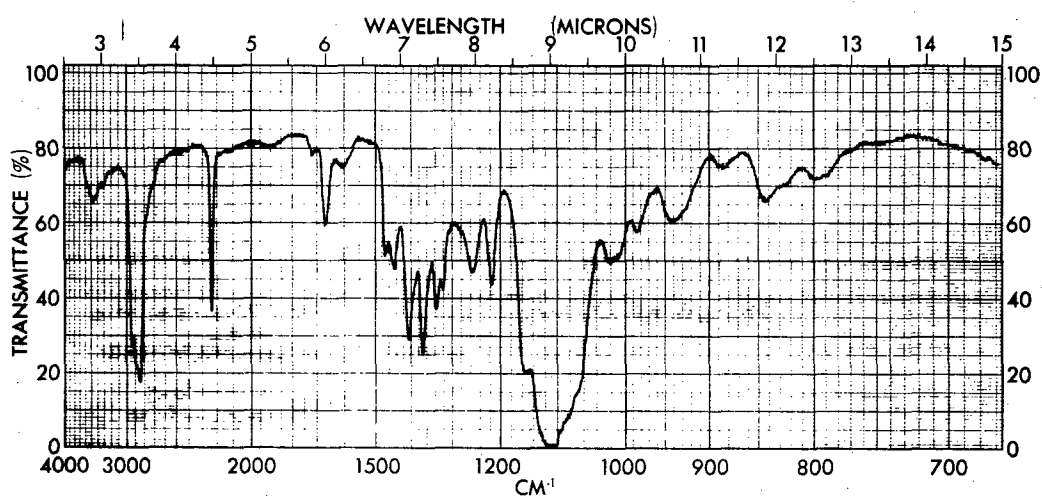


Figure 28 - Infrared Spectrum of 1,2-Di-(2-cyanoethoxy)propane (Liquid)

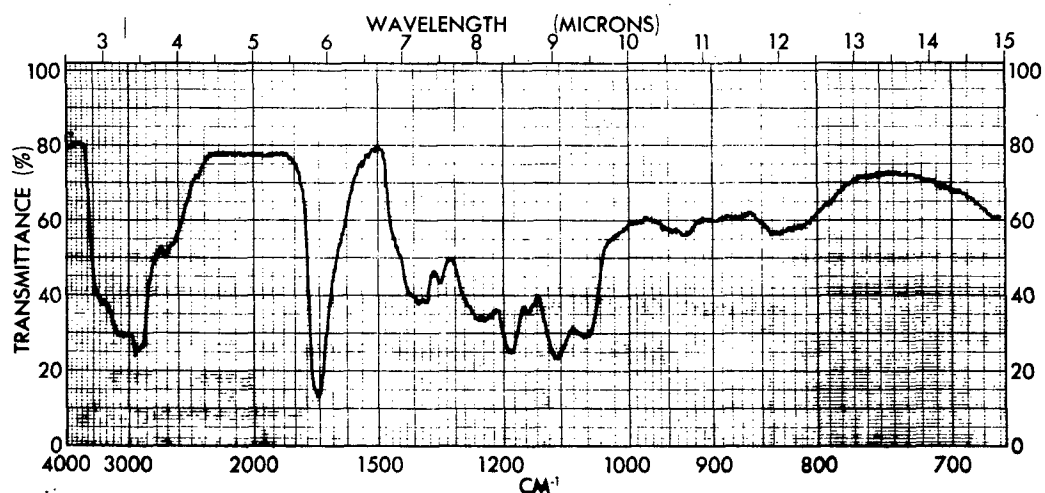


Figure 29 - Infrared Spectrum of 5-Methyl-4,7-dioxadecanedioic Acid (Liquid)

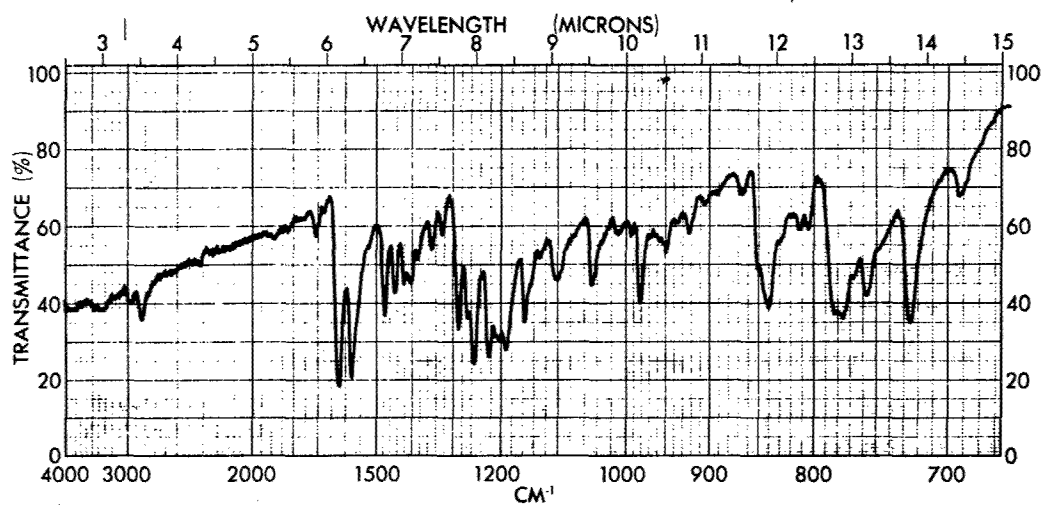
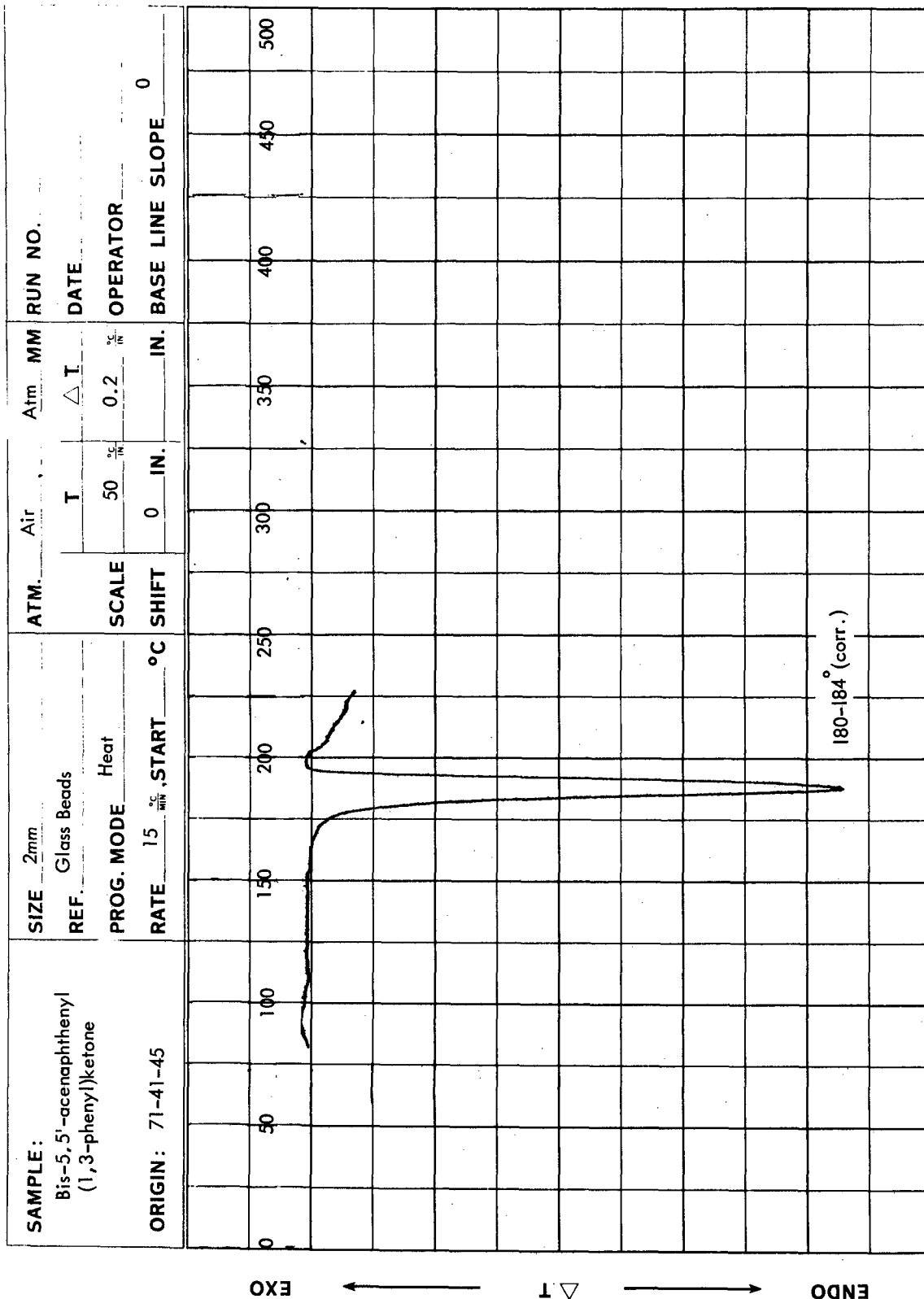


Figure 30 - Infrared Spectrum of Bis-5,5'-acenaphthenyl(1,3-phenyl)ketone (KBr)



T, $^{\circ}\text{C}$ (CHROMEL: ALUMEL)*

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 31 - DTA of Bis-5,5'-acenaphthényl(1,5-phenyl)ketone

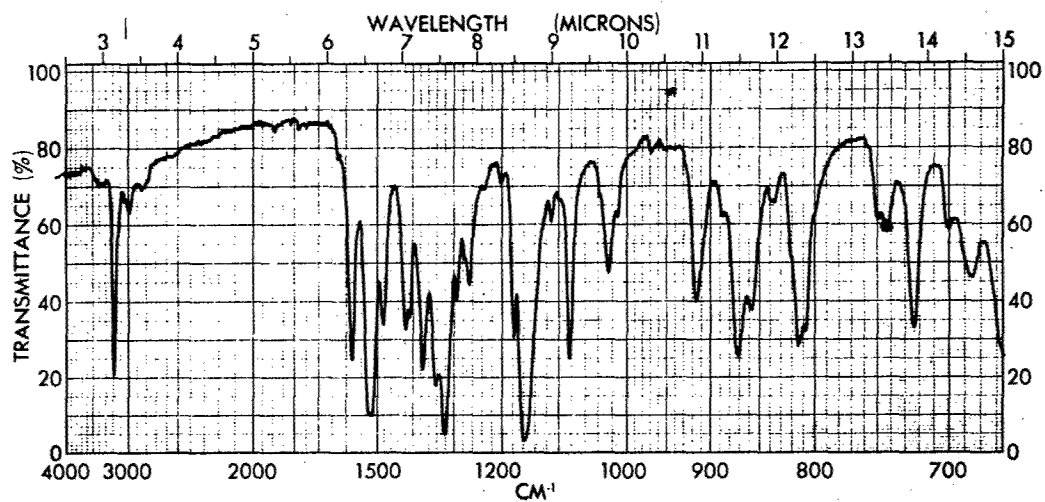
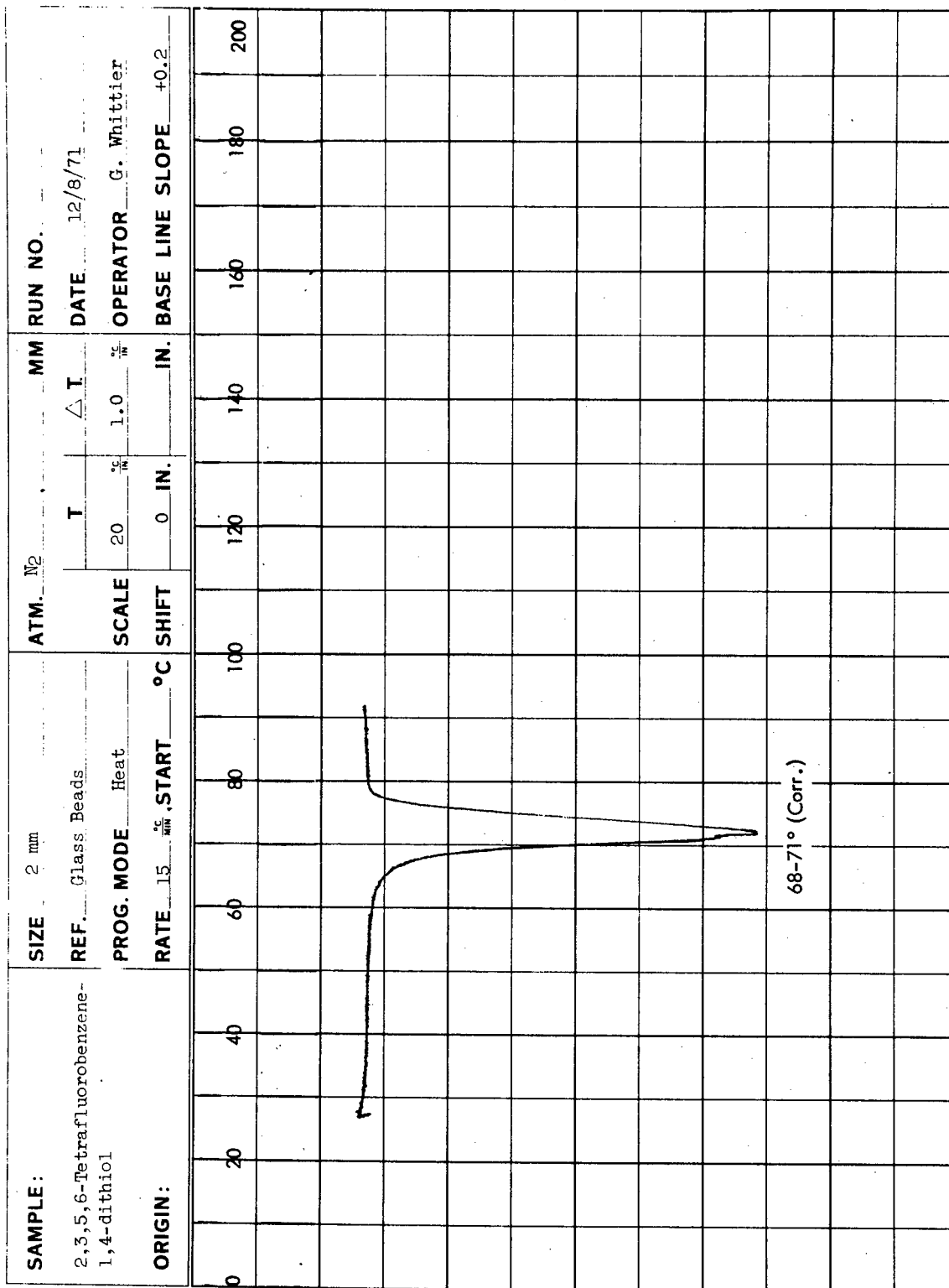


Figure 32 - Infrared Spectrum of 4,5-Dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide) (KBr)



T. °C (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 33 - DTA of 2,3,5,6-Tetrafluorobenzene-1,4-dithiol

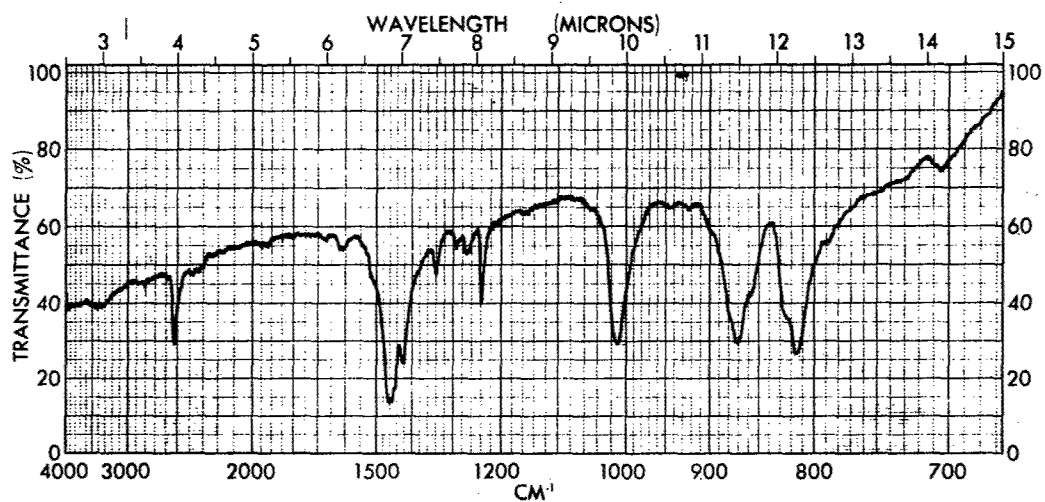


Figure 34 - Infrared Spectrum of 2,3,5,6-Tetrafluorobenzene-1,4-dithiol (KBr)

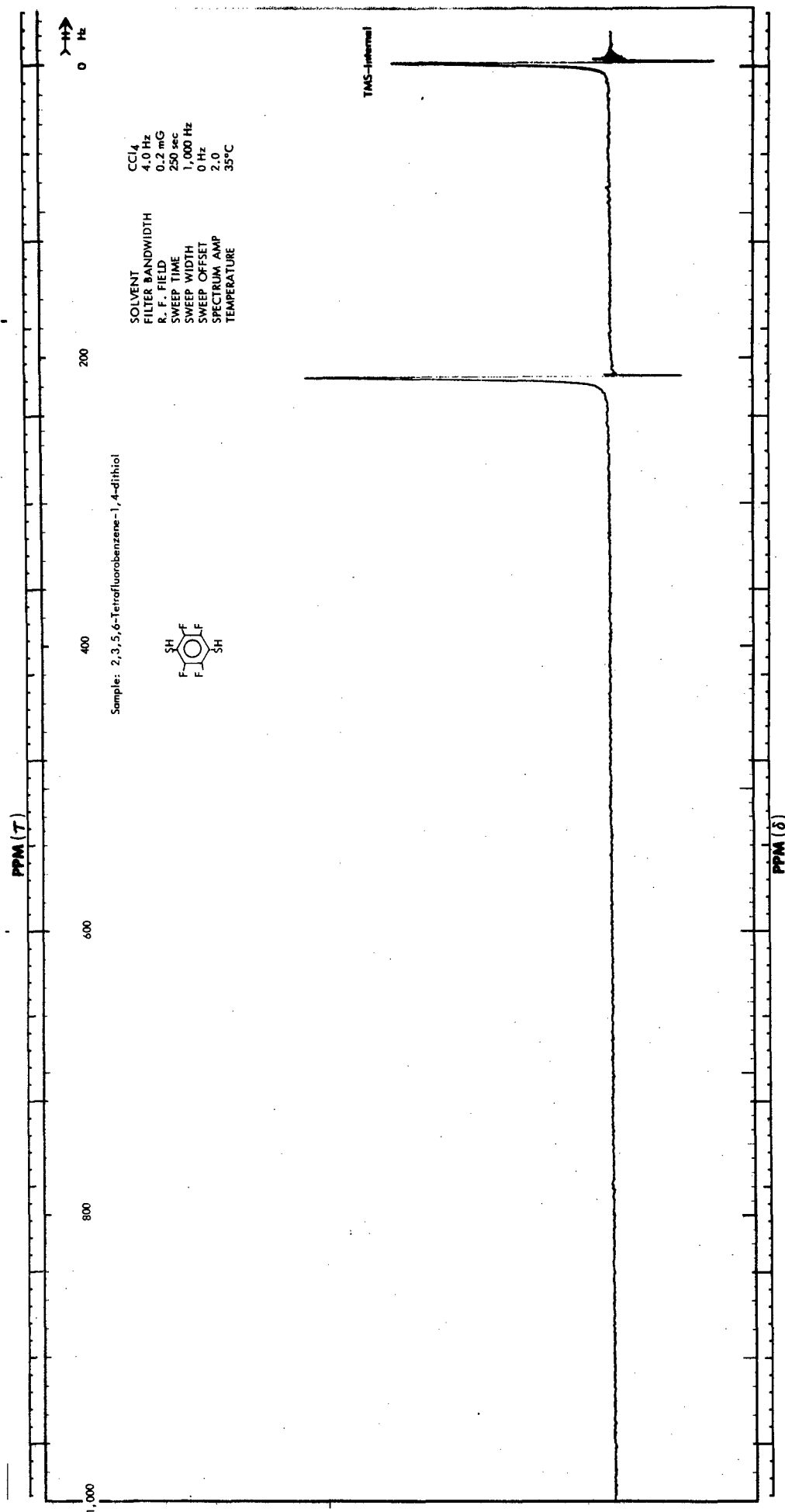


Figure 35 - NMR Spectrum of 2,3,5,6-Tetrafluorobenzene-1,4-dithiol

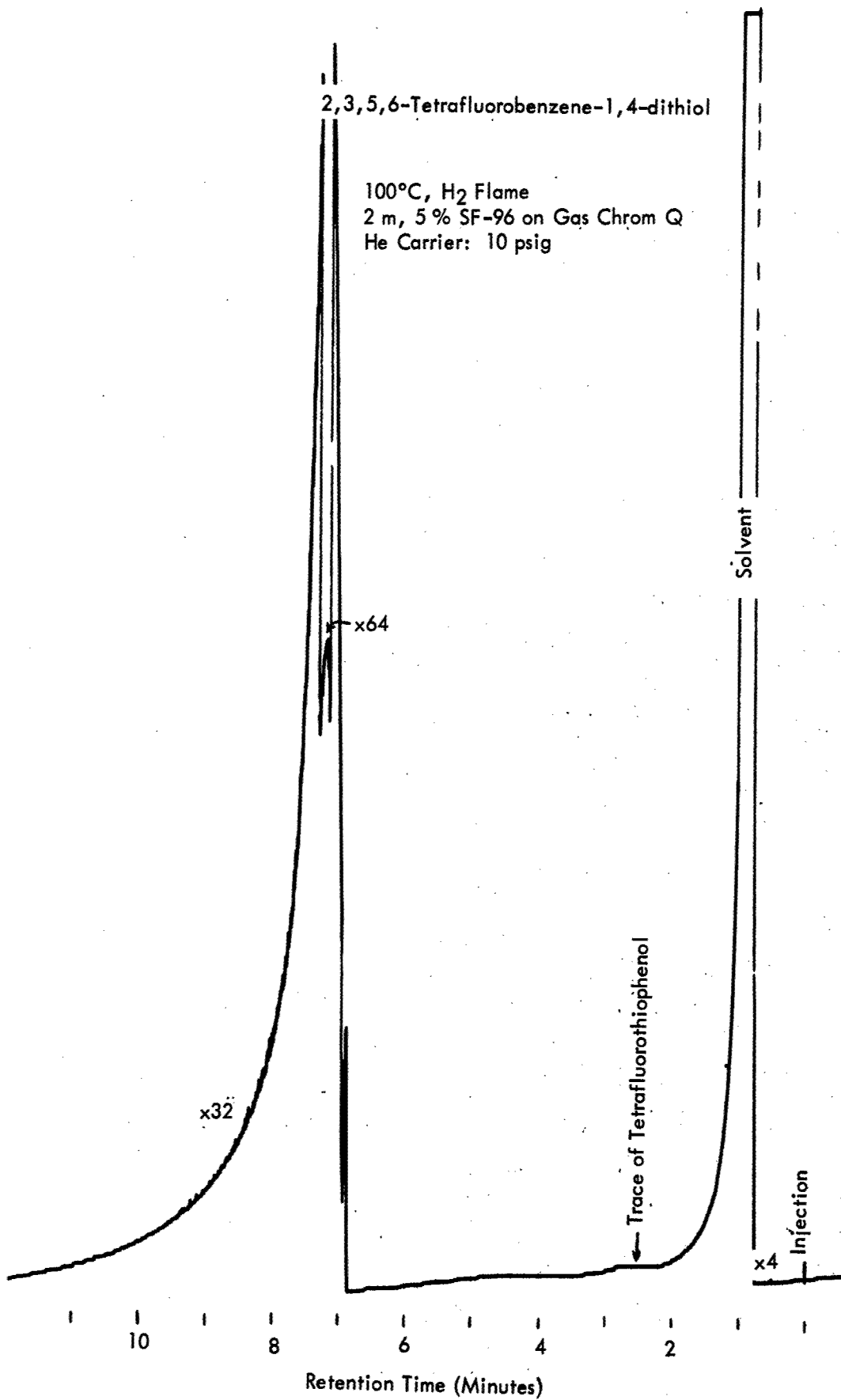


Figure 36 - Gas-Liquid Chromatogram of 2,3,5,6-Tetrafluorobenzene-1,4-dithiol

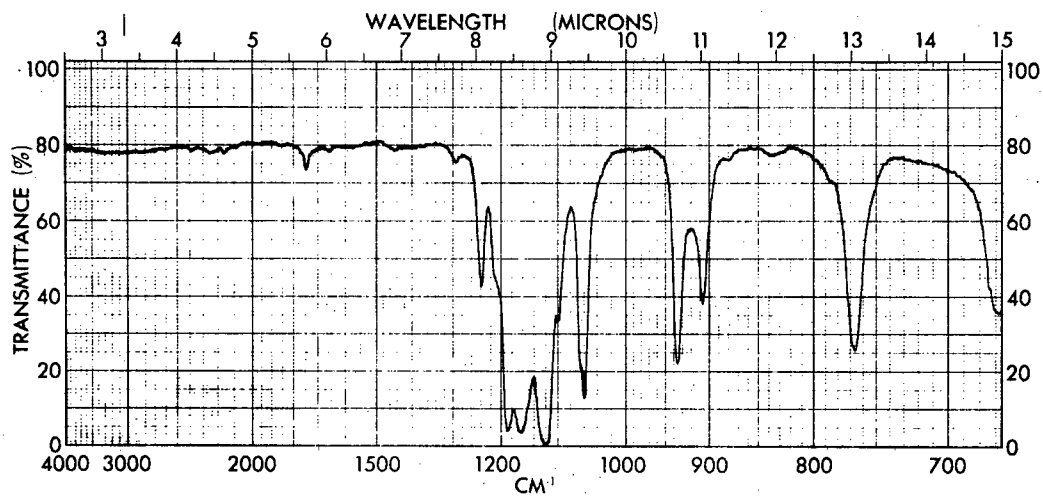


Figure 37 - Infrared Spectrum of 1,3-Diiodohexafluoropropane (Liquid)

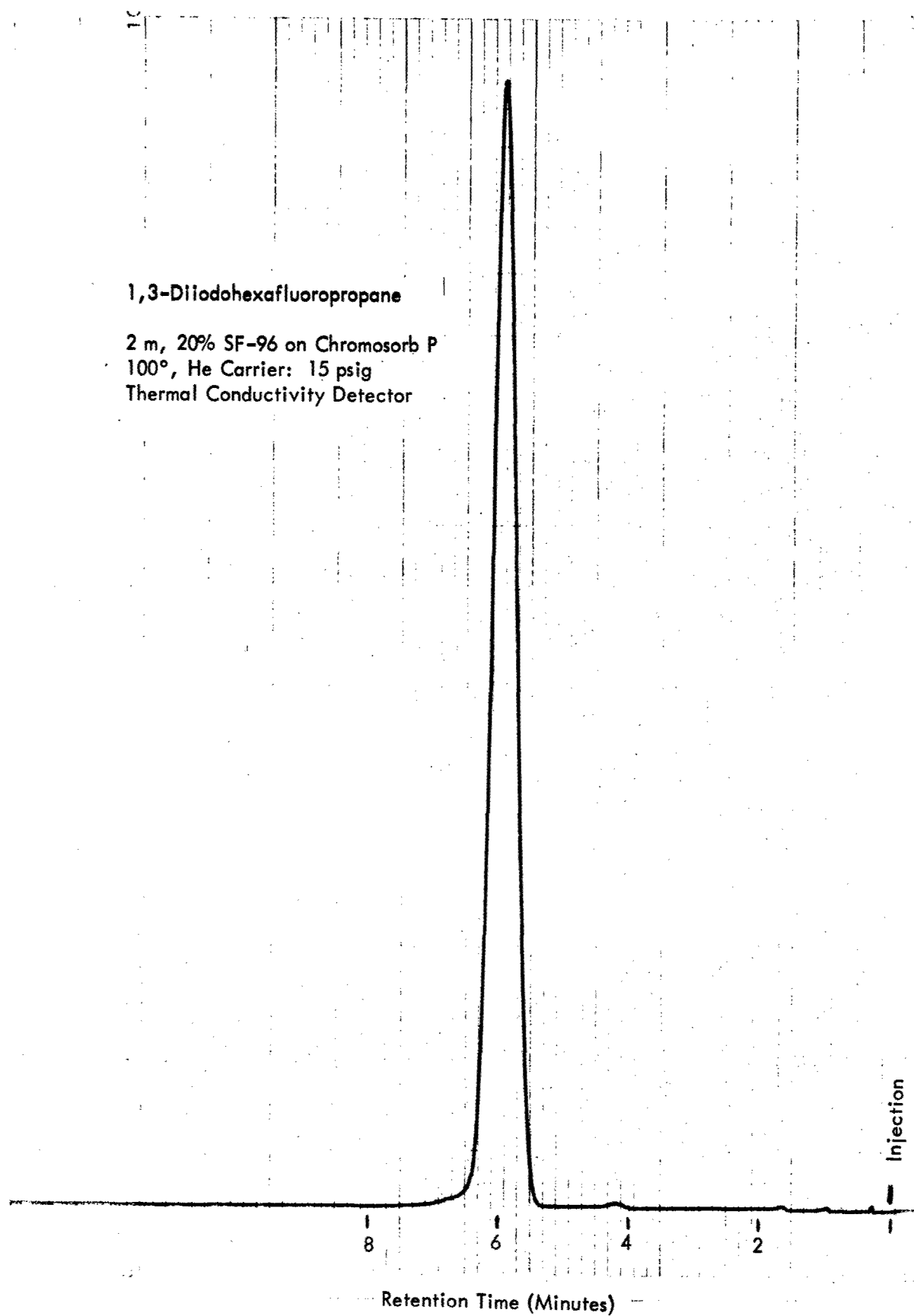


Figure 38 - Gas-Liquid Chromatogram of 1,3-Diiodohexafluoropropane

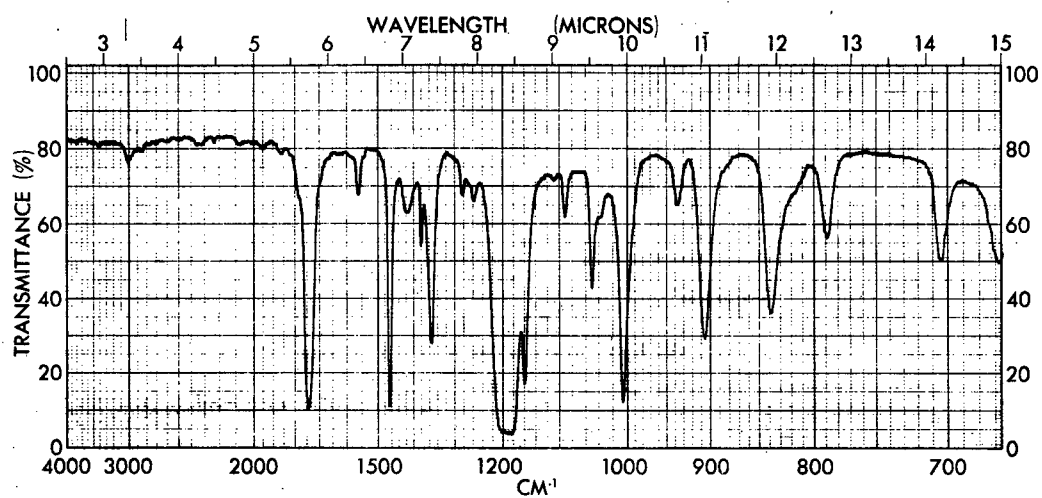


Figure 39 - Infrared Spectrum of 4-Iodophenyl Acetate (Liquid)

4-Iodophenylacetate

2m, 5% SF-96 on Gas ChromQ
140°, He carrier: 10 psig
Flame Ionization

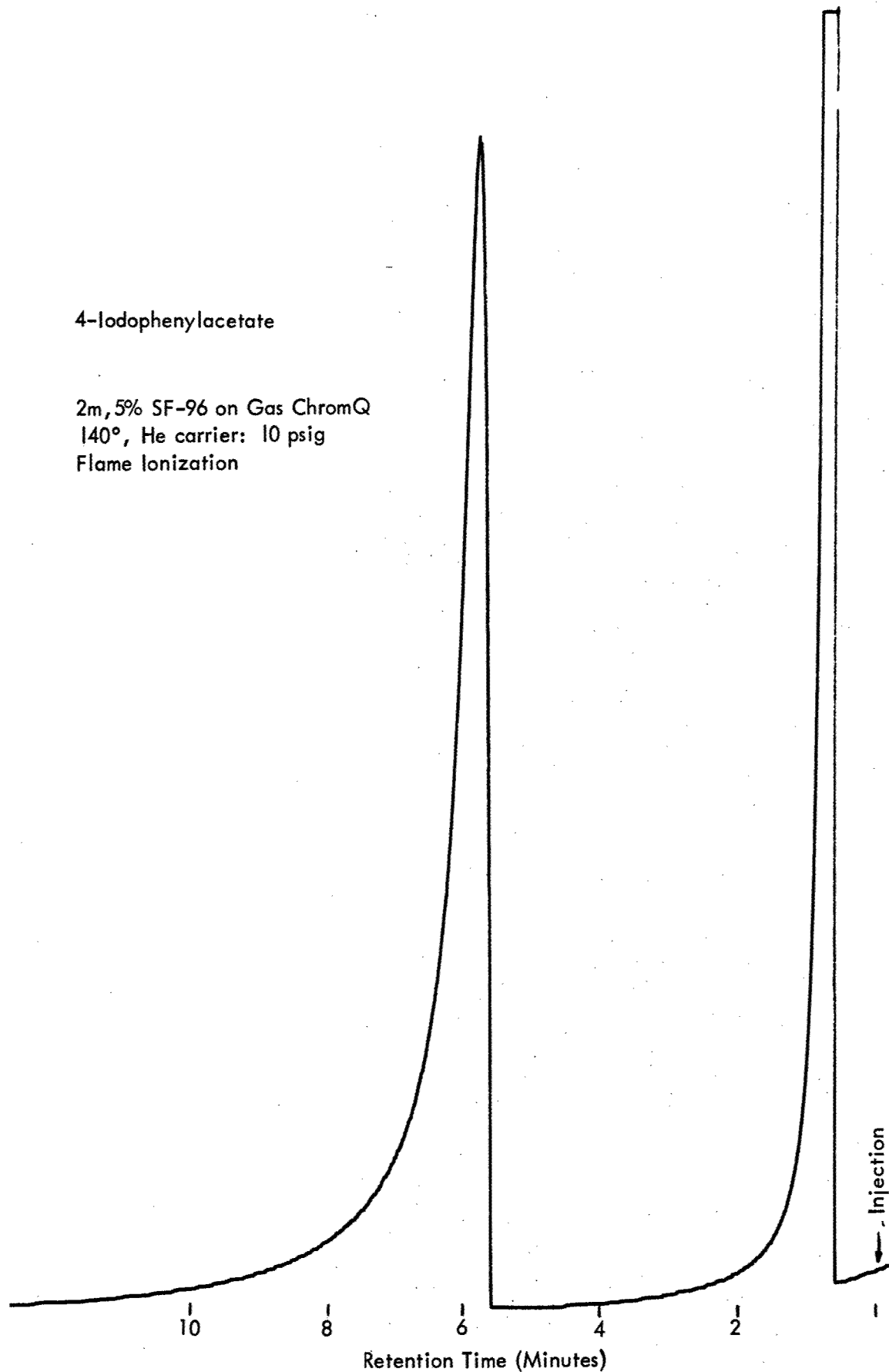


Figure 40 - Gas-Liquid Chromatogram of 4-Iodophenyl Acetate

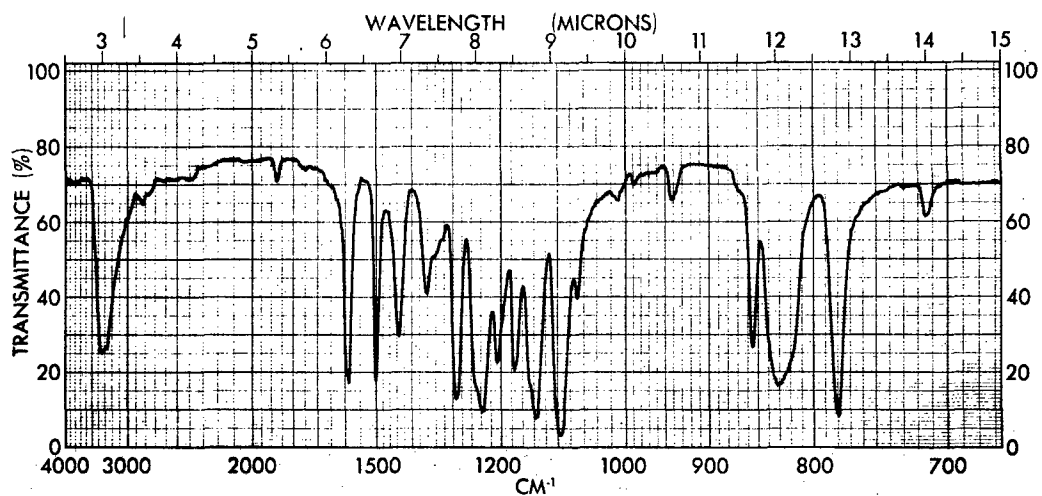
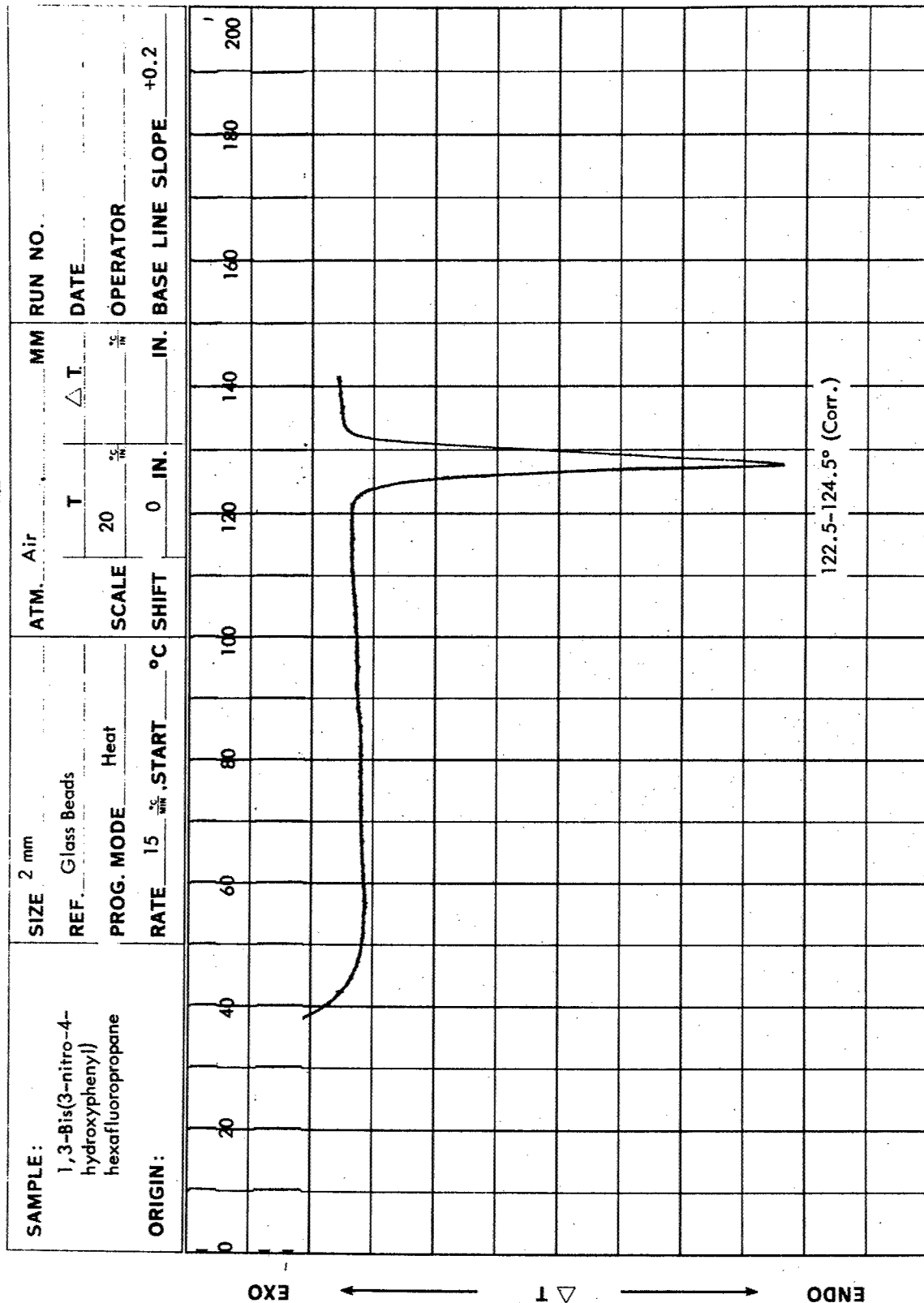


Figure 41 - Infrared Spectrum of 1,3-Bis(4-hydroxyphenyl)-hexafluoropropane (KBr)



T. °C (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 42 - DTA of 1,3-Bis(3-nitro-4-hydroxyphenyl)hexafluoropropane

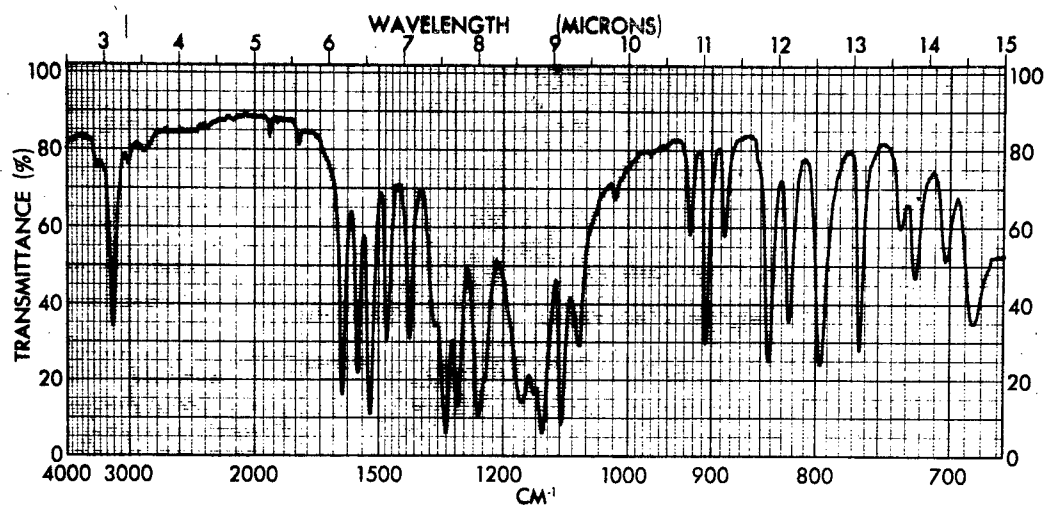


Figure 43 - Infrared Spectrum of 1,3-Bis(3-nitro-4-hydroxyphenyl)hexafluoropropane (KBr)

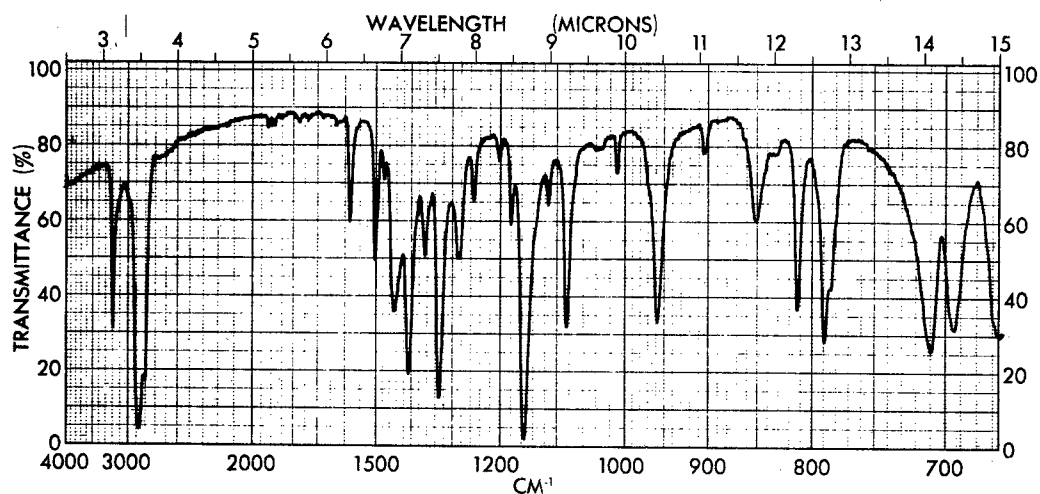


Figure 44 - Infrared Spectrum of 1,5-Bis(p-toluenesulfonamido)naphthalene (Nujol)

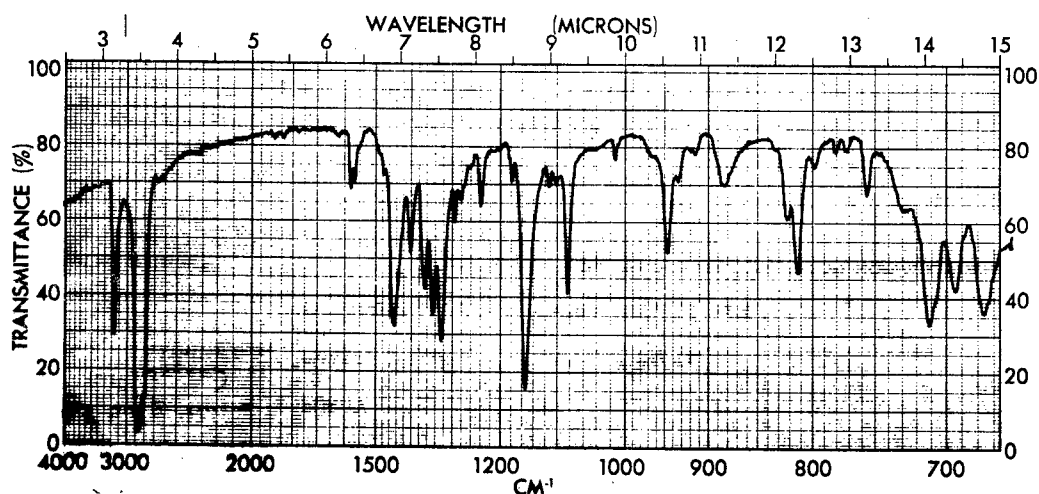


Figure 45 - Infrared Spectrum of 4,8-Dibromo-1,5-bis(p-toluenesulfonamido)naphthalene (Nujol)

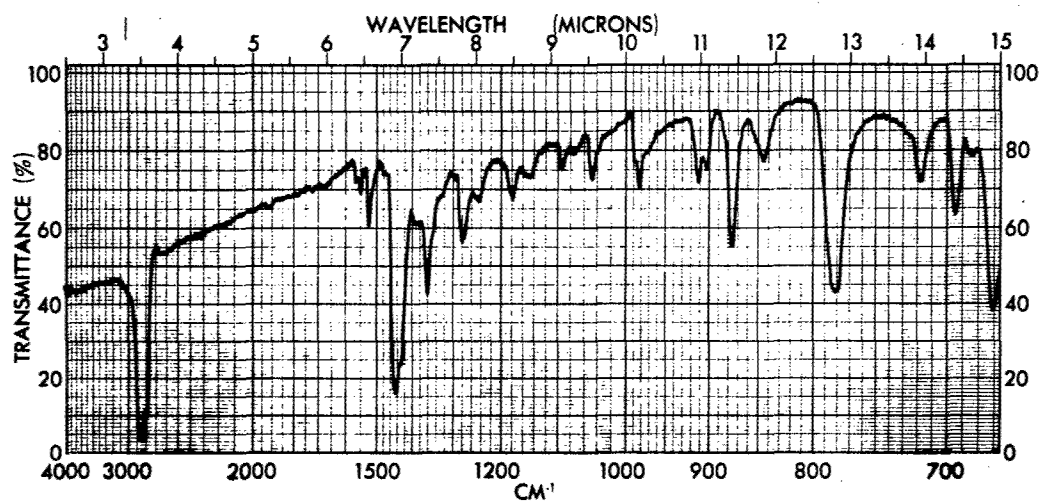
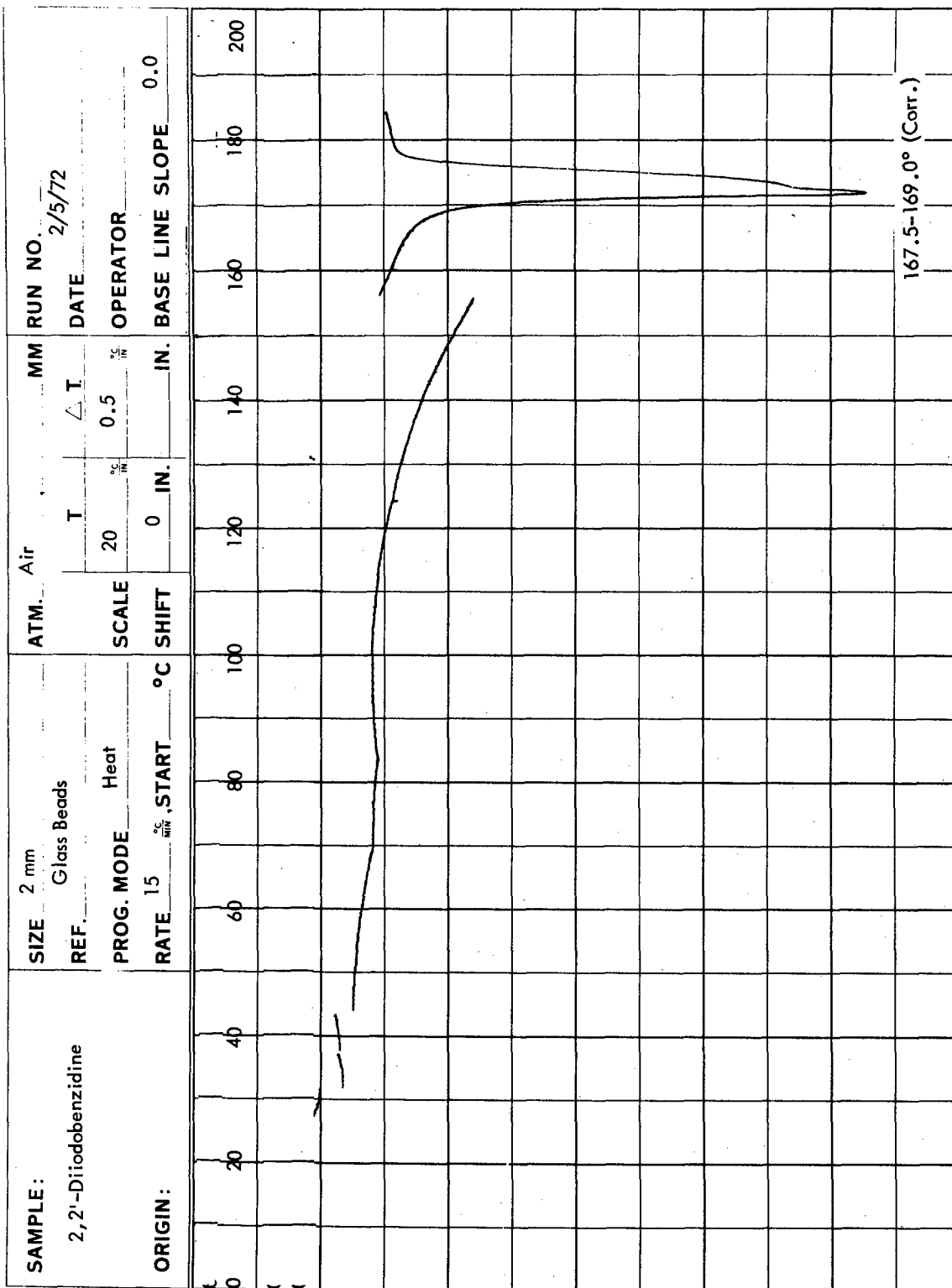


Figure 46 - Infrared Spectrum of 3,3'-Diiodoazoxybenzene (Nujol)



T, °C (CHROMEL: ALUMEL) *

Figure 47 - DTA of 2,2'-Diiodobenzidine

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

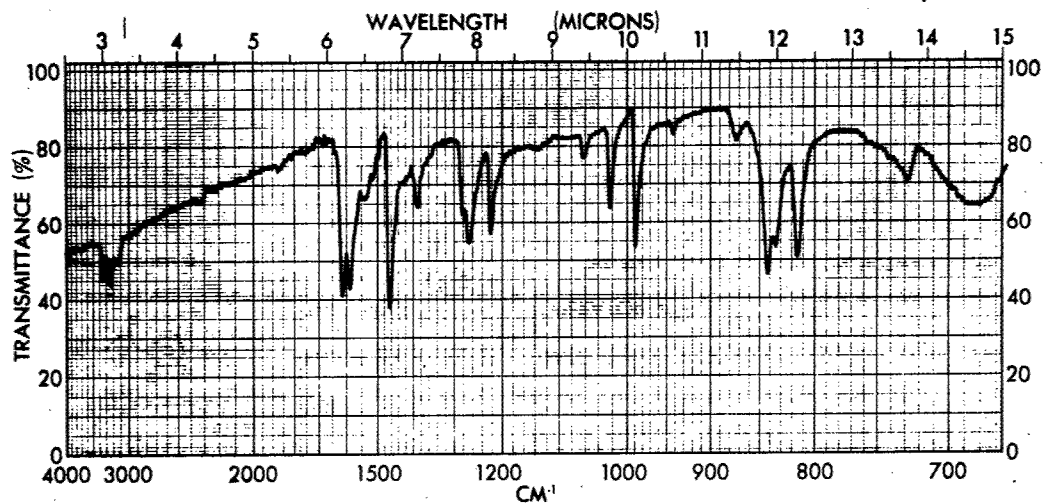


Figure 48 - Infrared Spectrum of 2,2'-Diiodobenzidine (KBr)

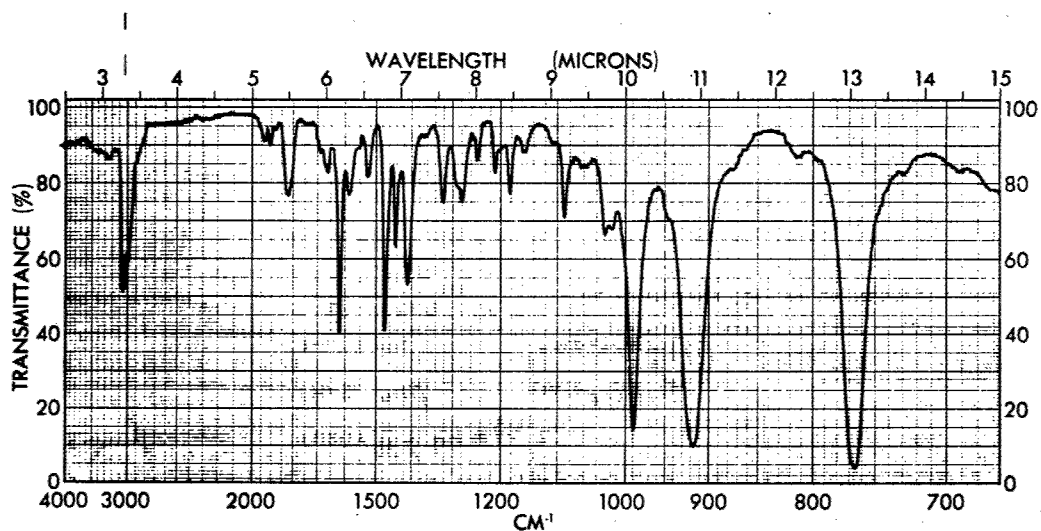


Figure 49 - Infrared Spectrum of o-Divinylbenzene (Liquid)

o-Divinylbenzene

2 m 5% SF-96 on Gas Chrom Q
125°, He Carrier: 8 psig
Flame Ionization Detector

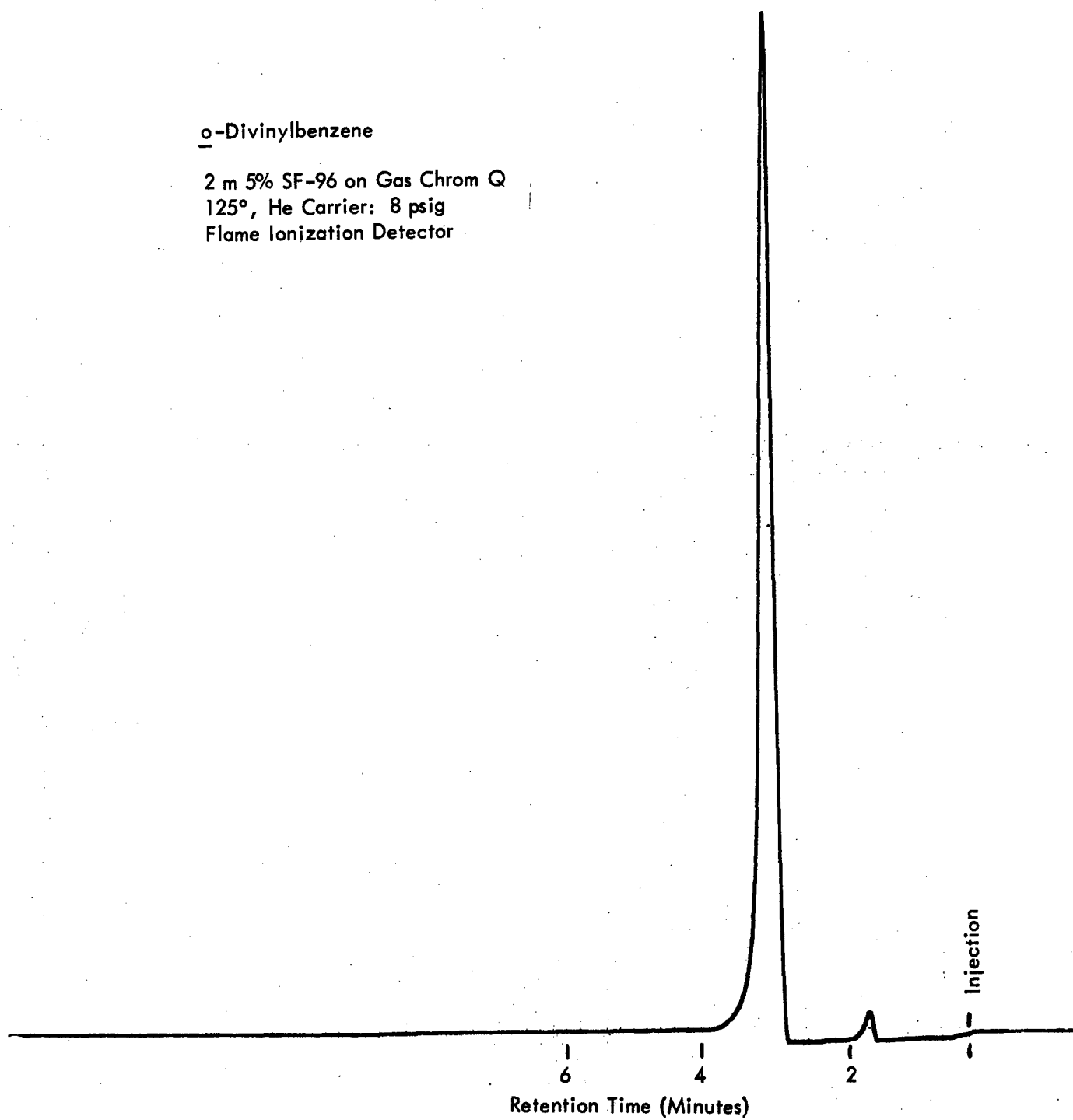


Figure 50 - Gas-Liquid Chromatogram of o-Divinylbenzene

80°C, H₂ Flame
2 m., 20% SF-96 on acid-washed Chromosorb P
He Carrier--10 psig

X16 Perfluoro-n-octyl iodide

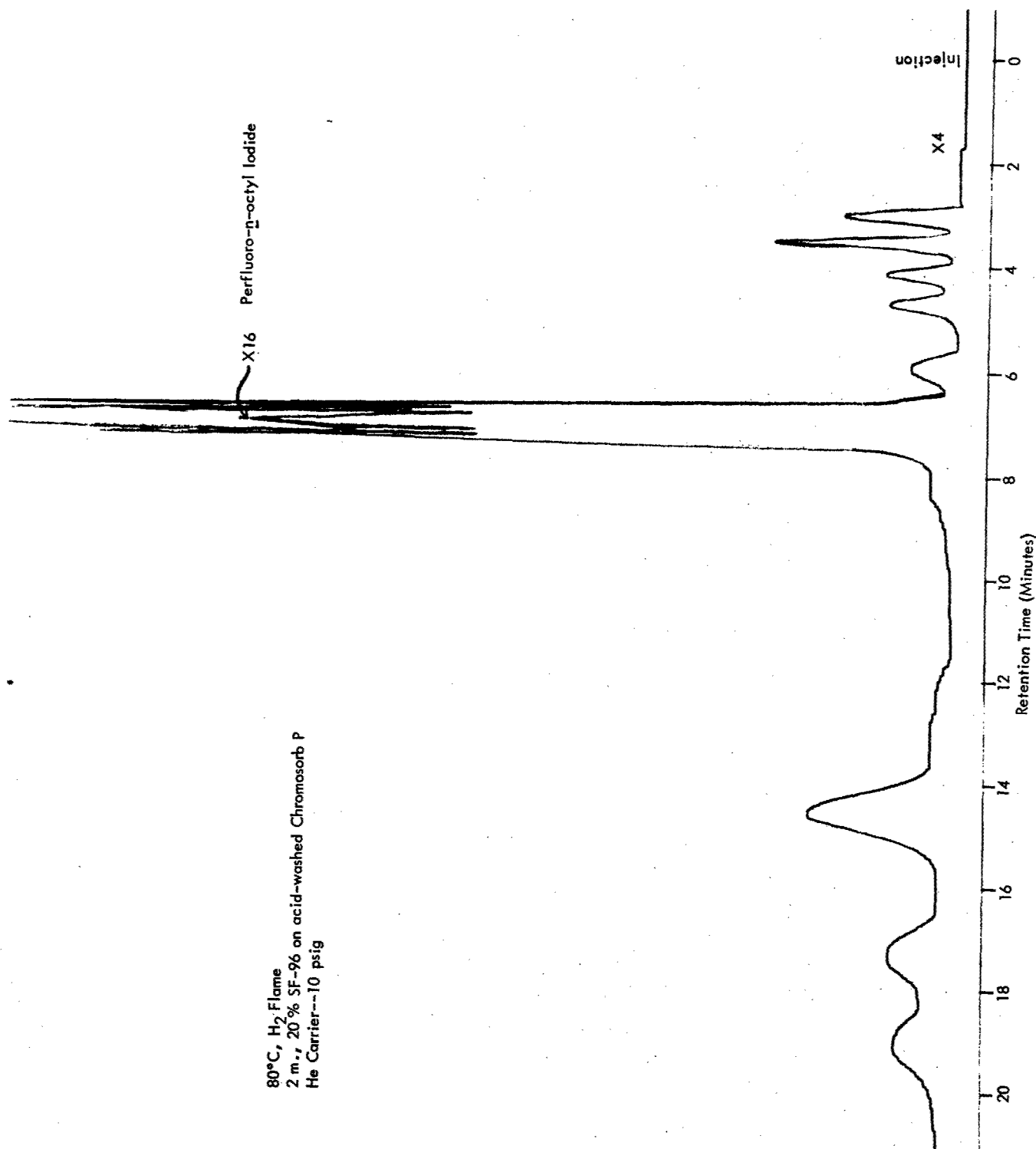


Figure 51 - Gas-Liquid Chromatogram of Starting Mixture of Perfluoroalkyl Iodides
(~ 78% Perfluoro-n-octyl Iodide)

80°C, H₂ Flame
2 m., 20% SF-96 on acid-washed Chromosorb P
He Carrier--10 psig

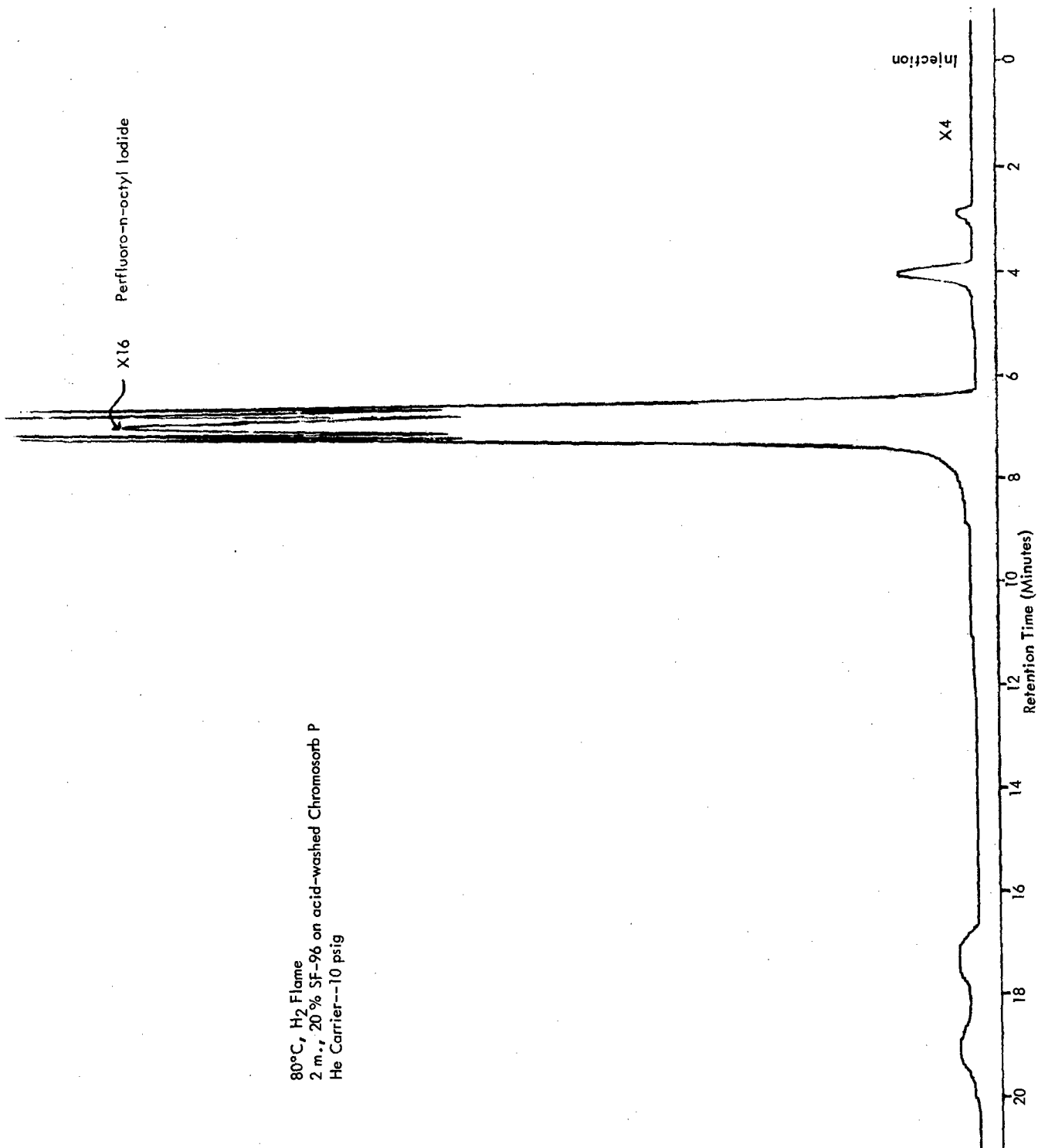


Figure 52 - Gas-Liquid Chromatogram of Perfluoro-n-octyl iodide (95-97.5% Pure)

80°C, H₂ Flame
2 m., 20% SF-96 on acid-washed Chromosorb P
He Carrier--10 psig

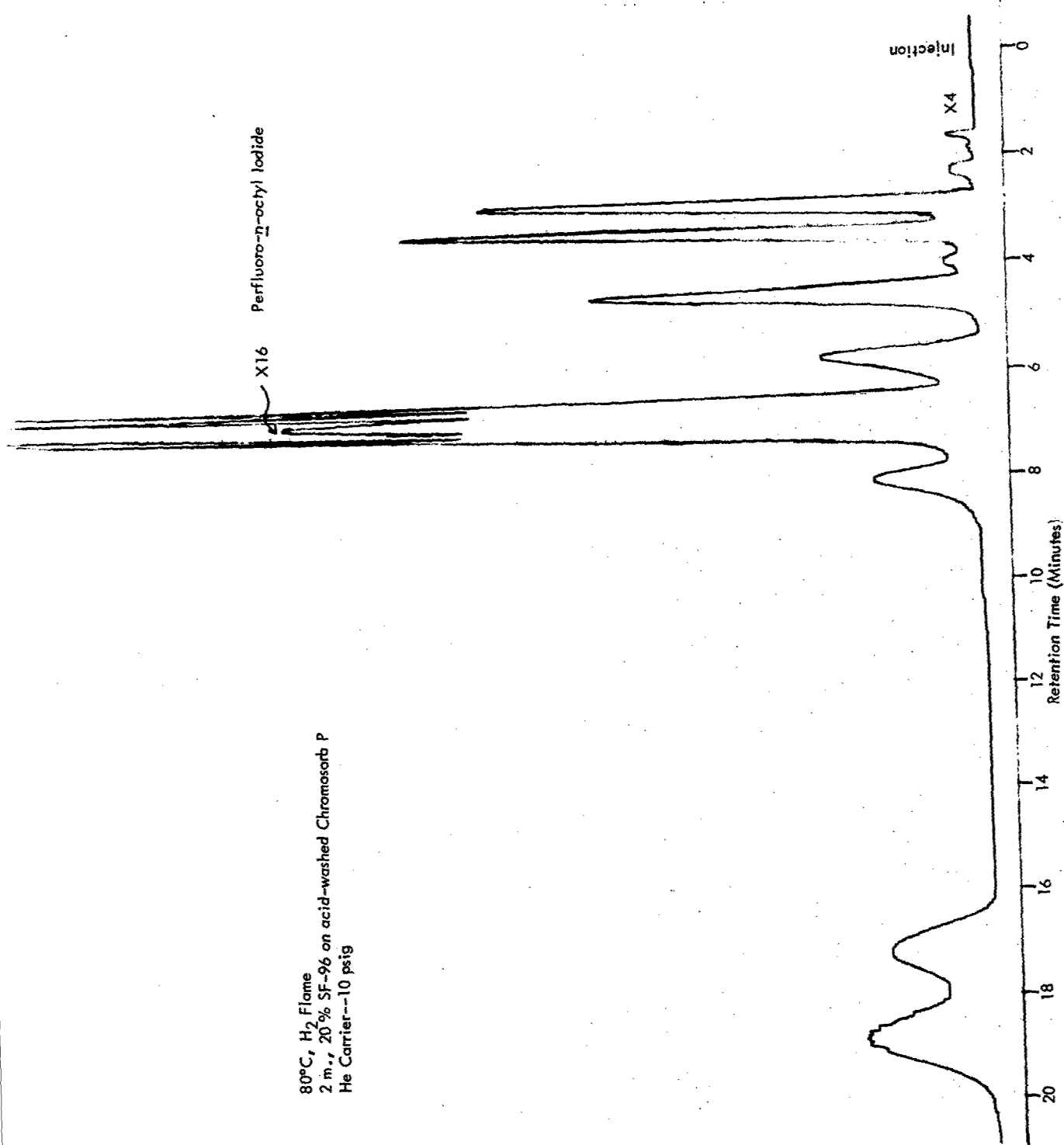


Figure 53 - Gas-Liquid Chromatogram of Lower-Boiling Fraction of Perfluoroalkyl Iodide Mixture

80°C, H₂ Flame
2 m., 20% SF-96 on acid-washed Chromosorb P
He Carrier--10 psig

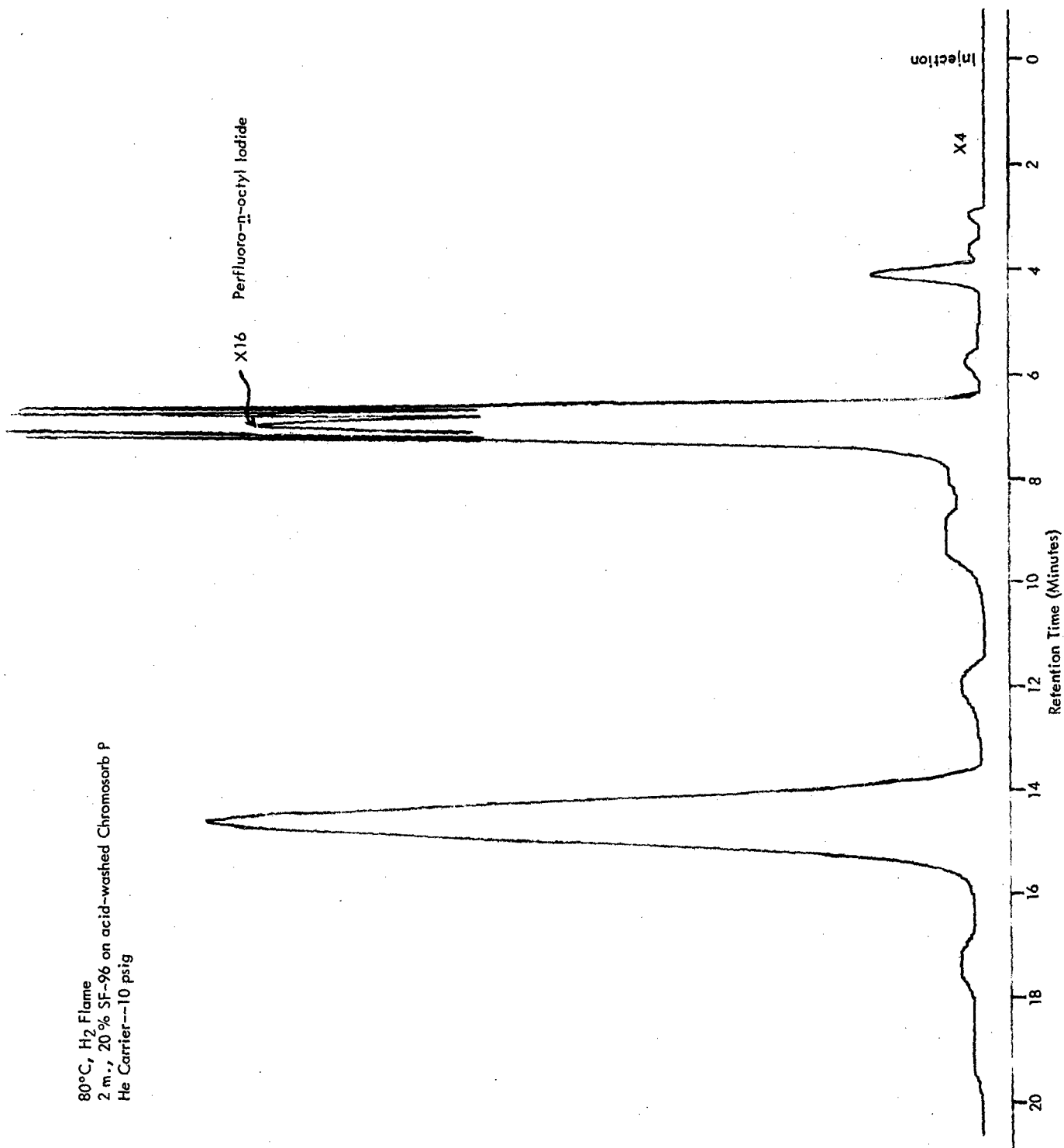


Figure 54 - Gas-Liquid Chromatogram of Higher-Boiling Fraction of Perfluoroalkyl Iodide Mixture

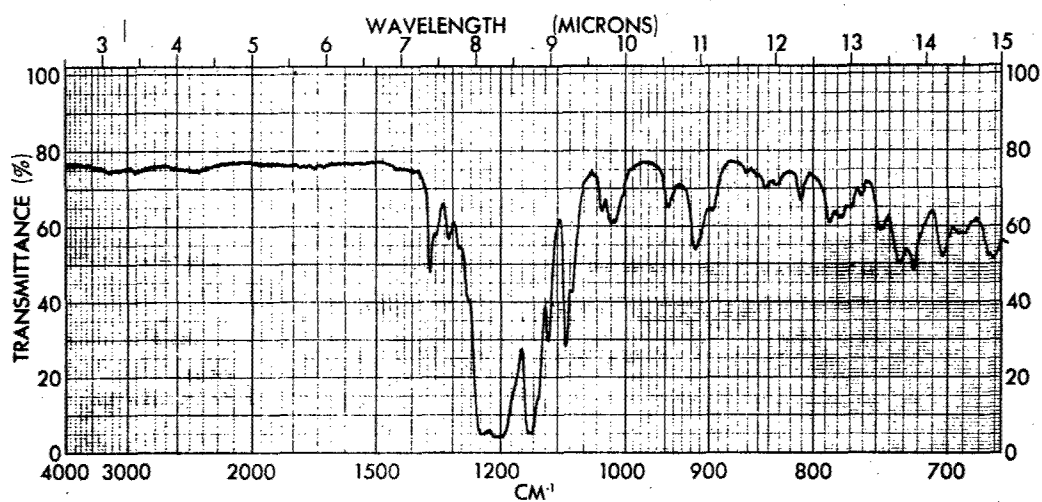


Figure 55 - Infrared Spectrum of Perfluoro-n-octyl Iodide (Liquid)

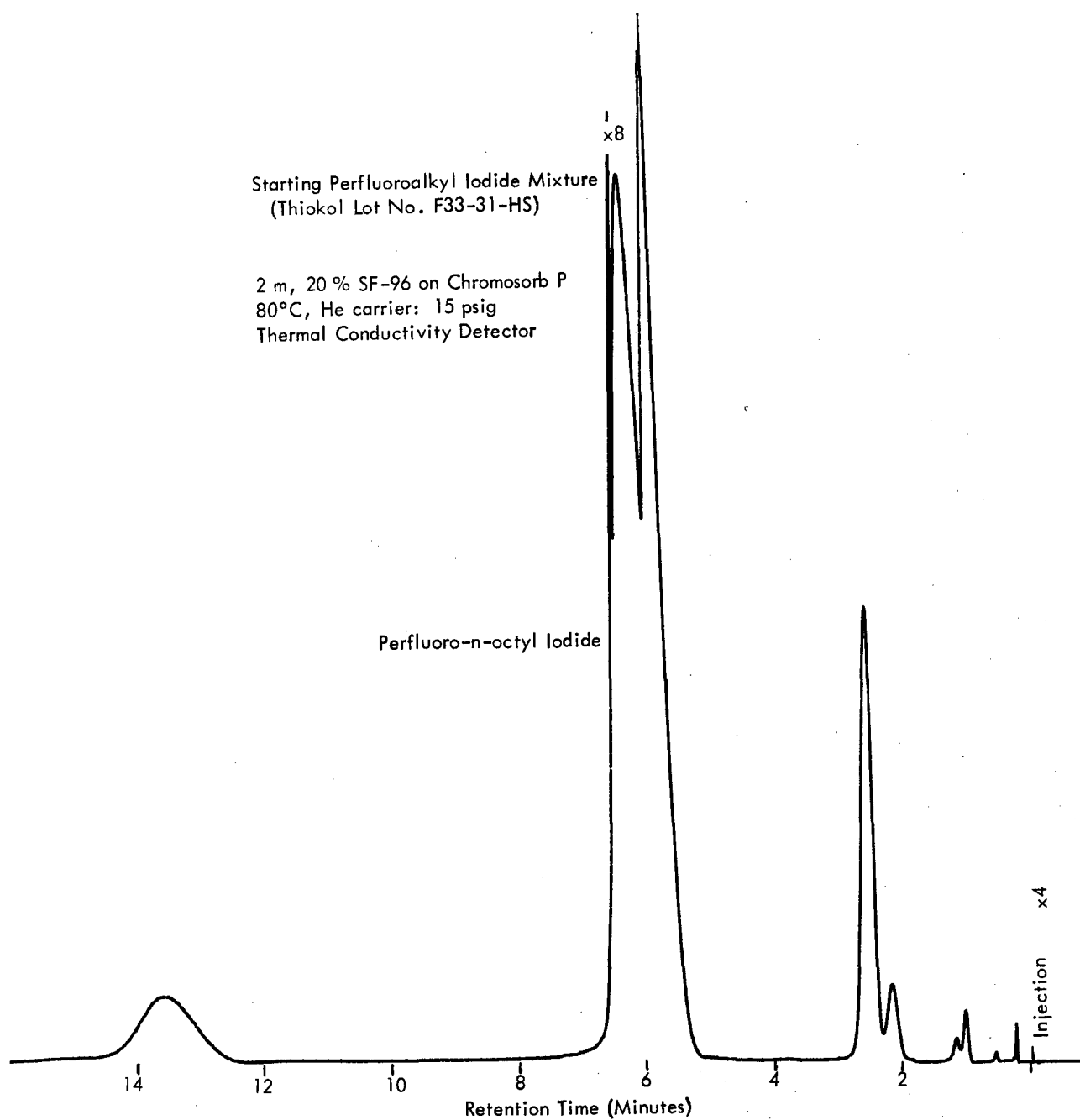


Figure 56 - Gas-Liquid Chromatogram of Starting Mixture of Perfluoro-alkyl Iodides (~ 84% Perfluoro-n-octyl Iodide)

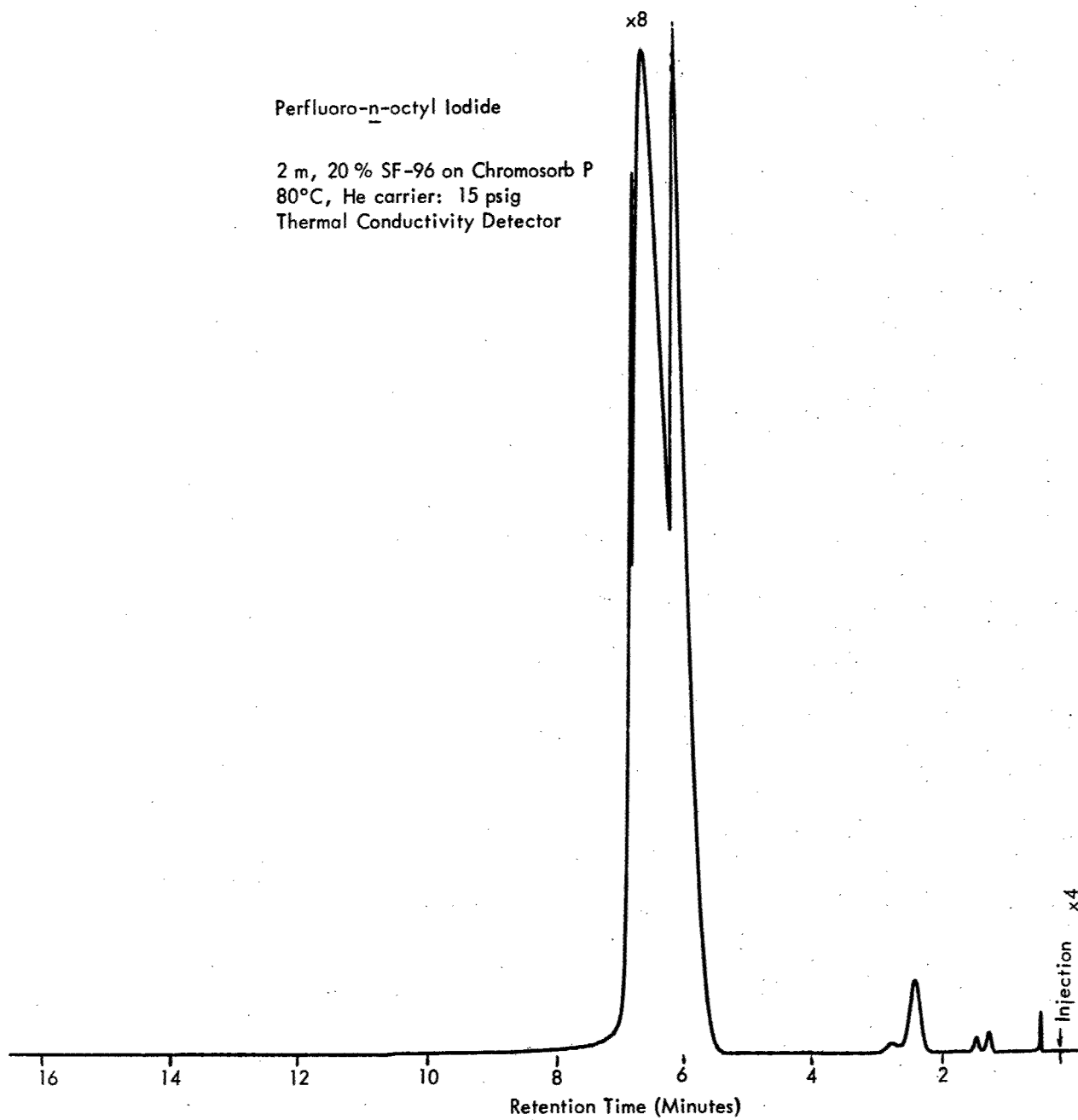


Figure 57 - Gas-Liquid Chromatogram of Perfluoro-n-octyl Iodide
(98.6% Pure)

Lower Boiling Fraction of
Perfluoroalkyl Iodide Mixture

2 m, 20 % SF-96 on Chromosorb P
80°C, He carrier: 15 psig
Thermal Conductivity Detector

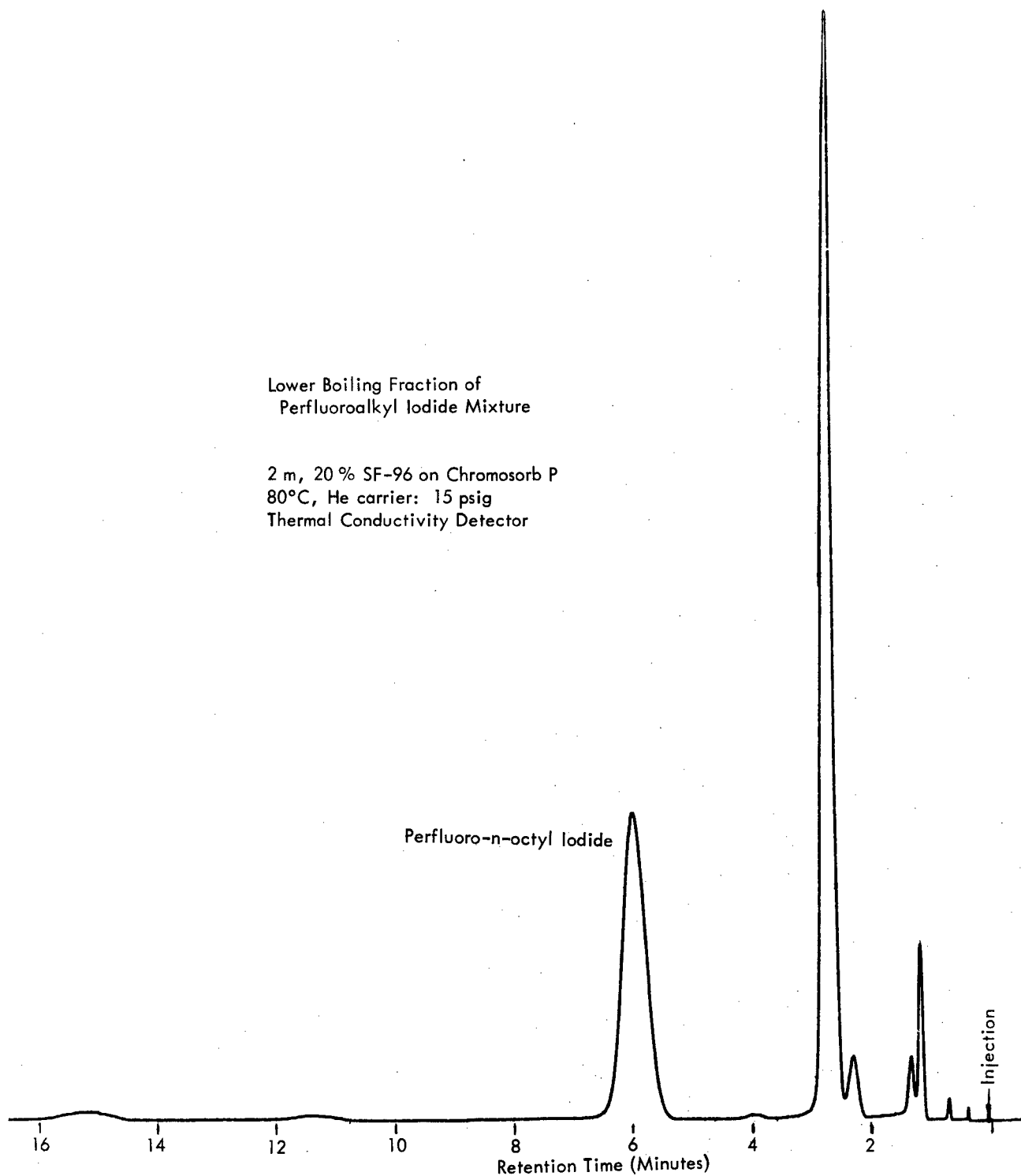


Figure 58 - Gas-Liquid Chromatogram of Lower-Boiling Fraction
of Perfluoroalkyl Iodide Mixture

Distillation Residue of
Perfluoroalkyl Iodide Mixture

2 m, 20 % SF-96 on Chromosorb P
80°C, He carrier: 15 psig
Thermal conductivity Detector

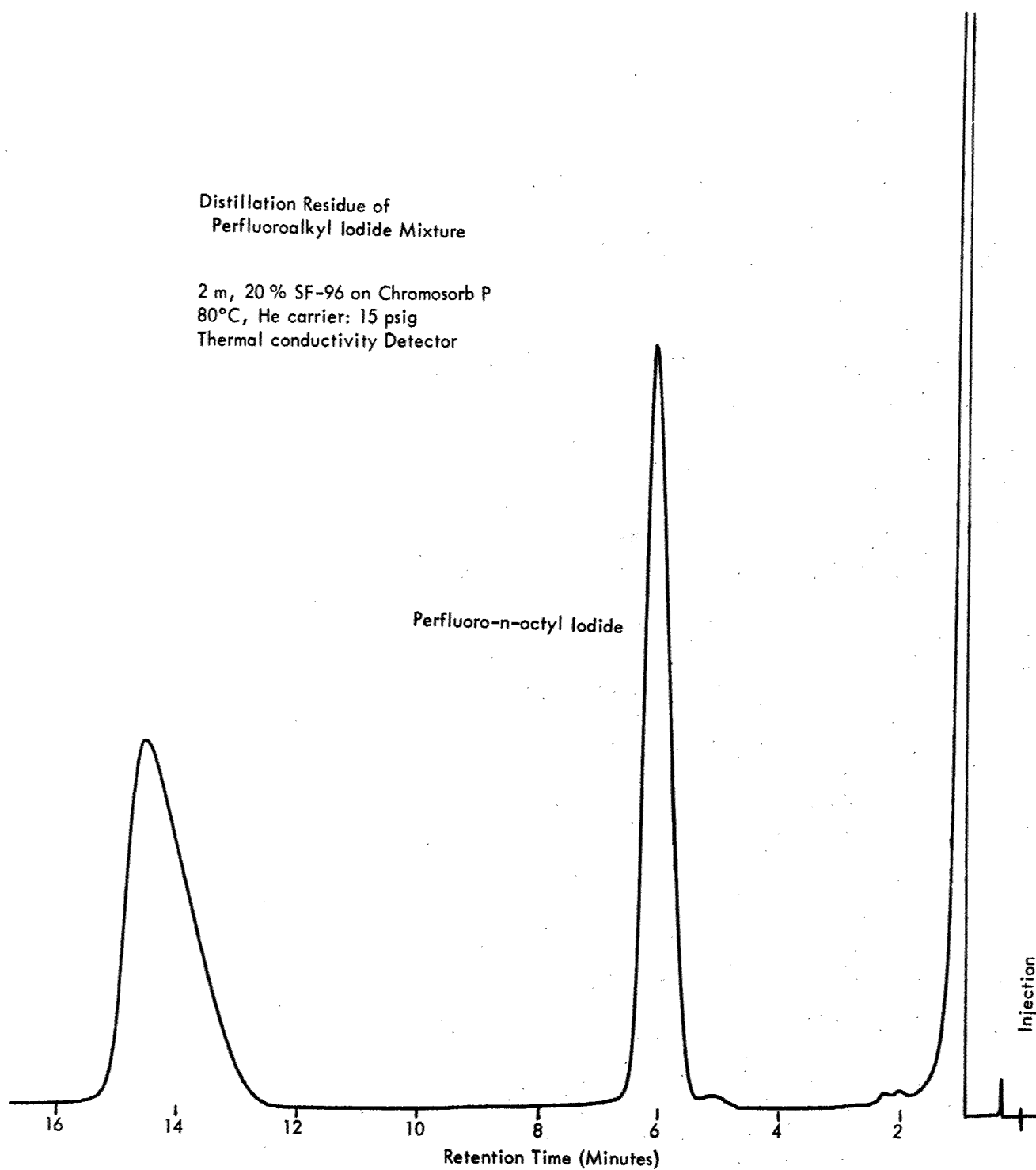


Figure 59 - Gas-Liquid Chromatogram of Distillation Residue
from Perfluoroalkyl Iodide Mixture

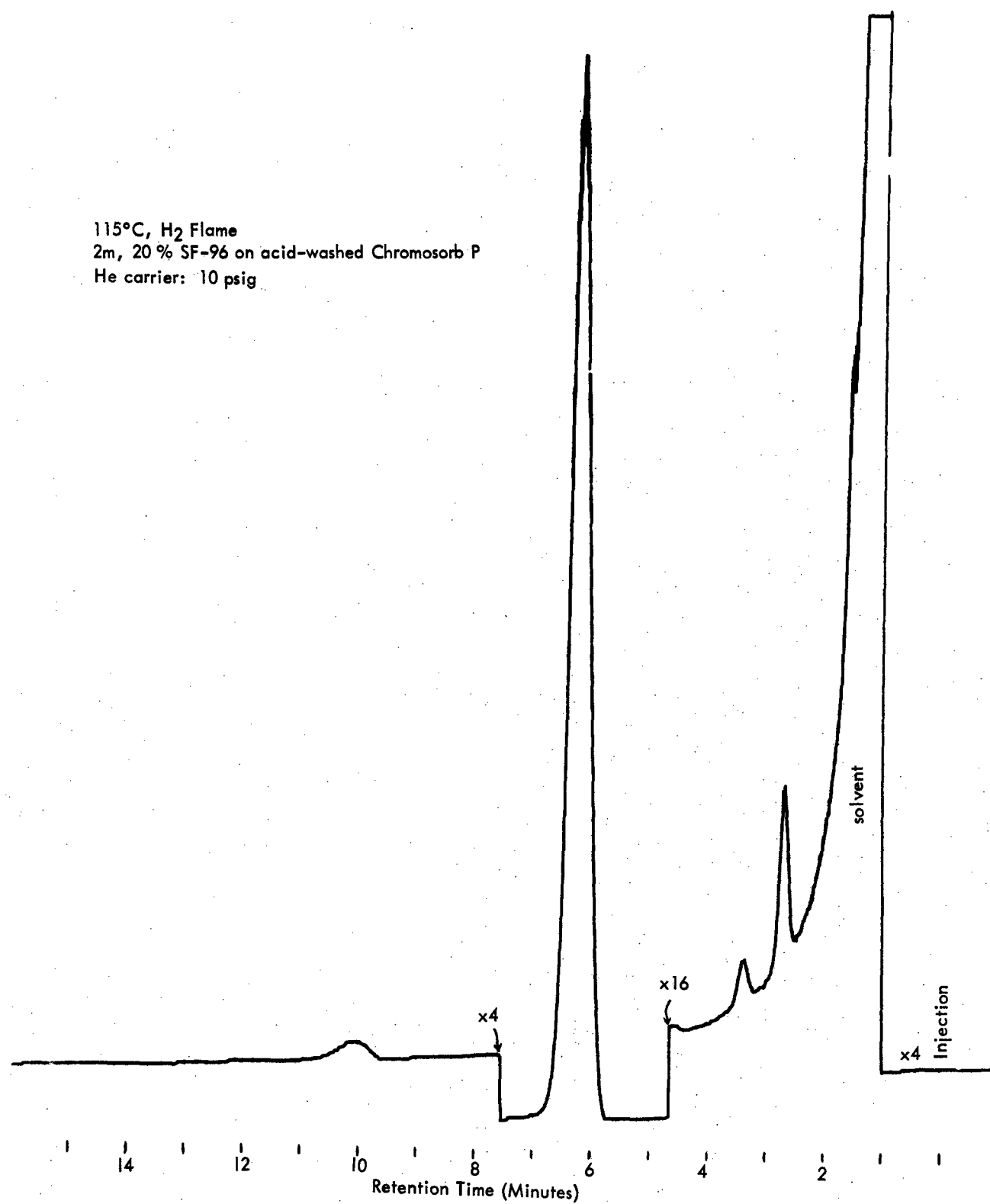
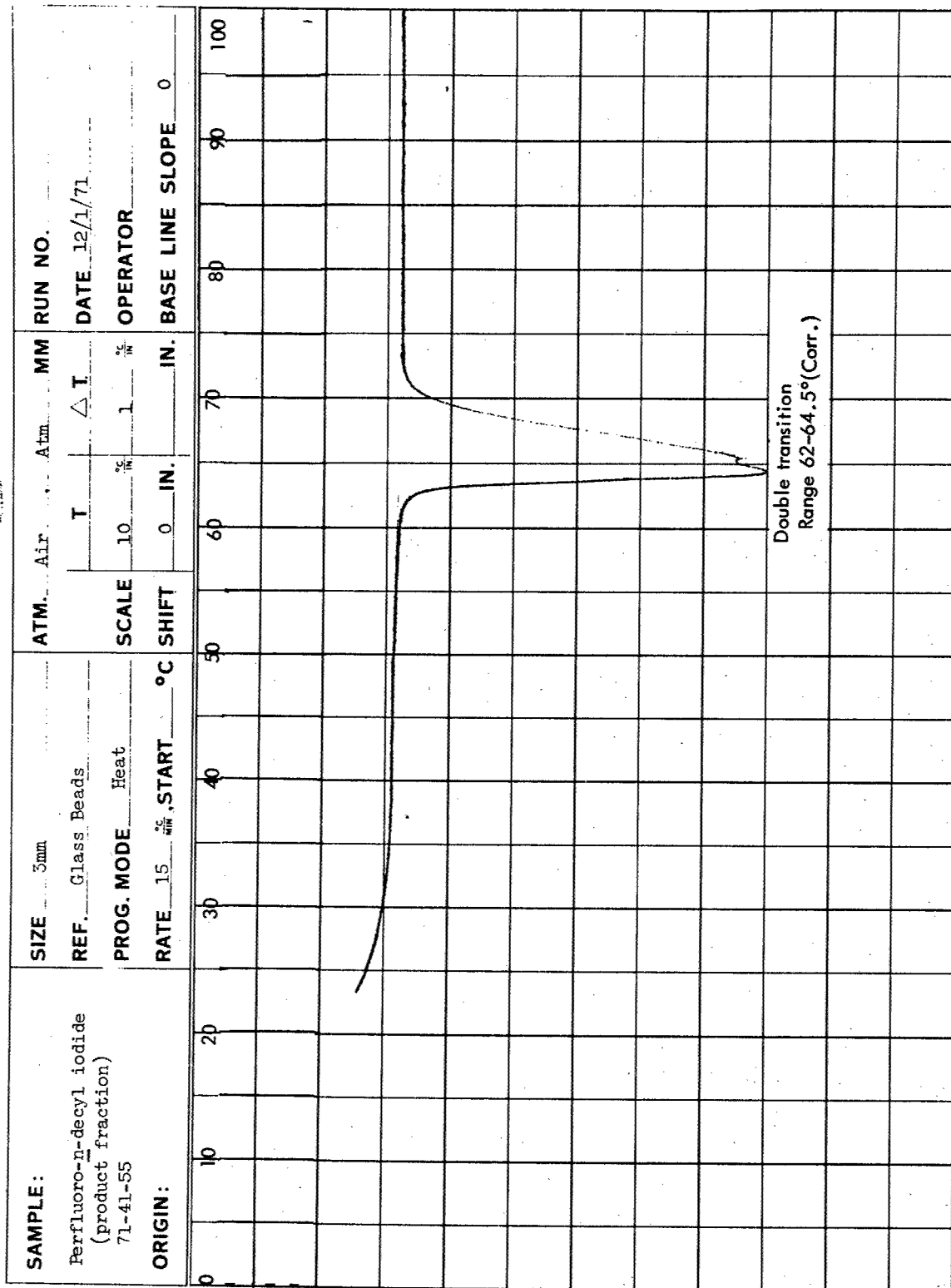


Figure 60 - Gas-Liquid Chromatogram of Starting Mixture
(Perfluoro-n-decyl Iodide, 97.0% Pure)



T. °C (CHROMEL: ALUMEL) *

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 61 - DTA of Perfluoro-n-decyl Iodide

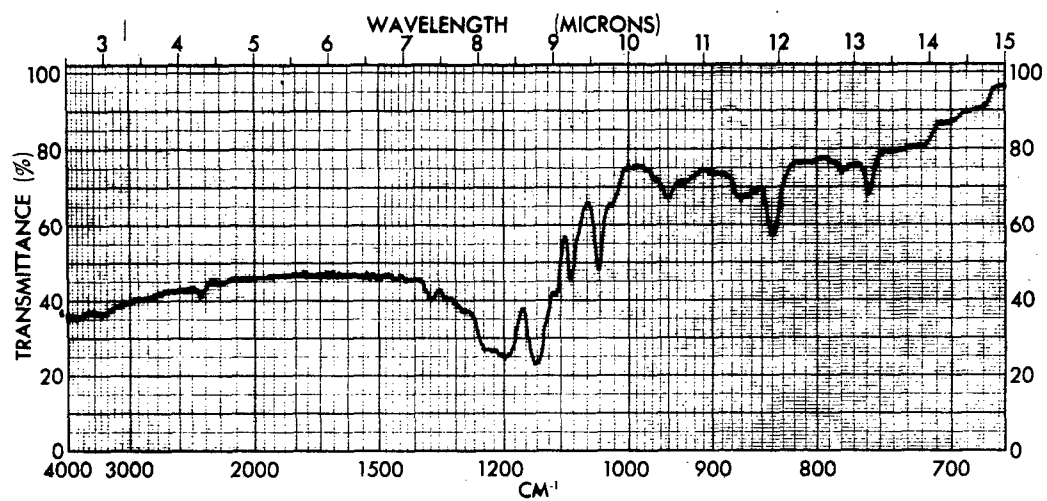


Figure 62 - Infrared Spectrum of Perfluoro-n-decyl Iodide (KBr)

115°C, H₂ Flame
2m, 20 % SF-96 on acid-washed Chromosorb P
He carrier: 10 psig

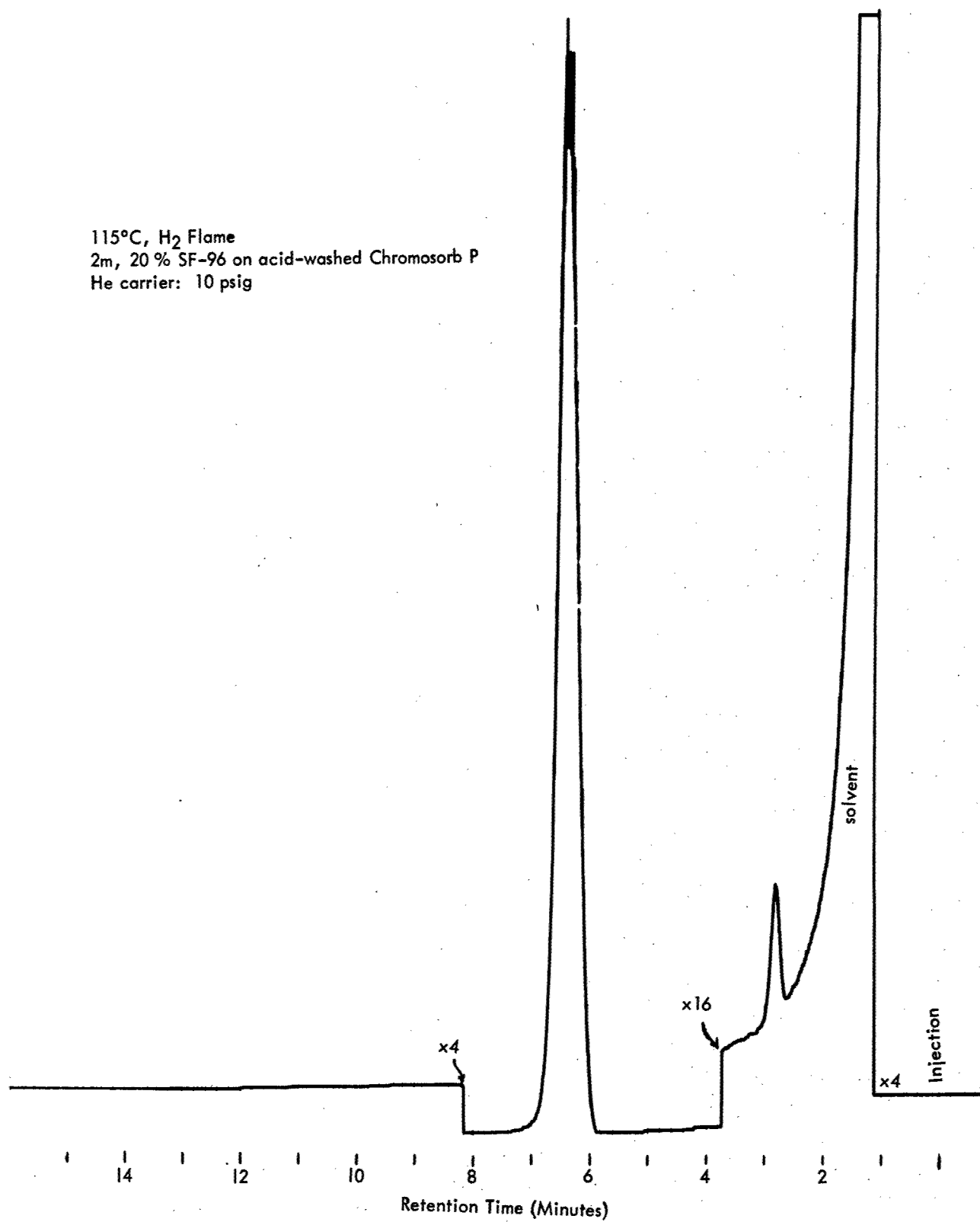


Figure 63 - Gas-Liquid Chromatogram of Perfluoro-n-decyl Iodide
(98.8% Pure)

115°C, H₂ Flame
2m, 20 % SF-96 on acid-washed Chromosorb P
He carrier: 10 psig

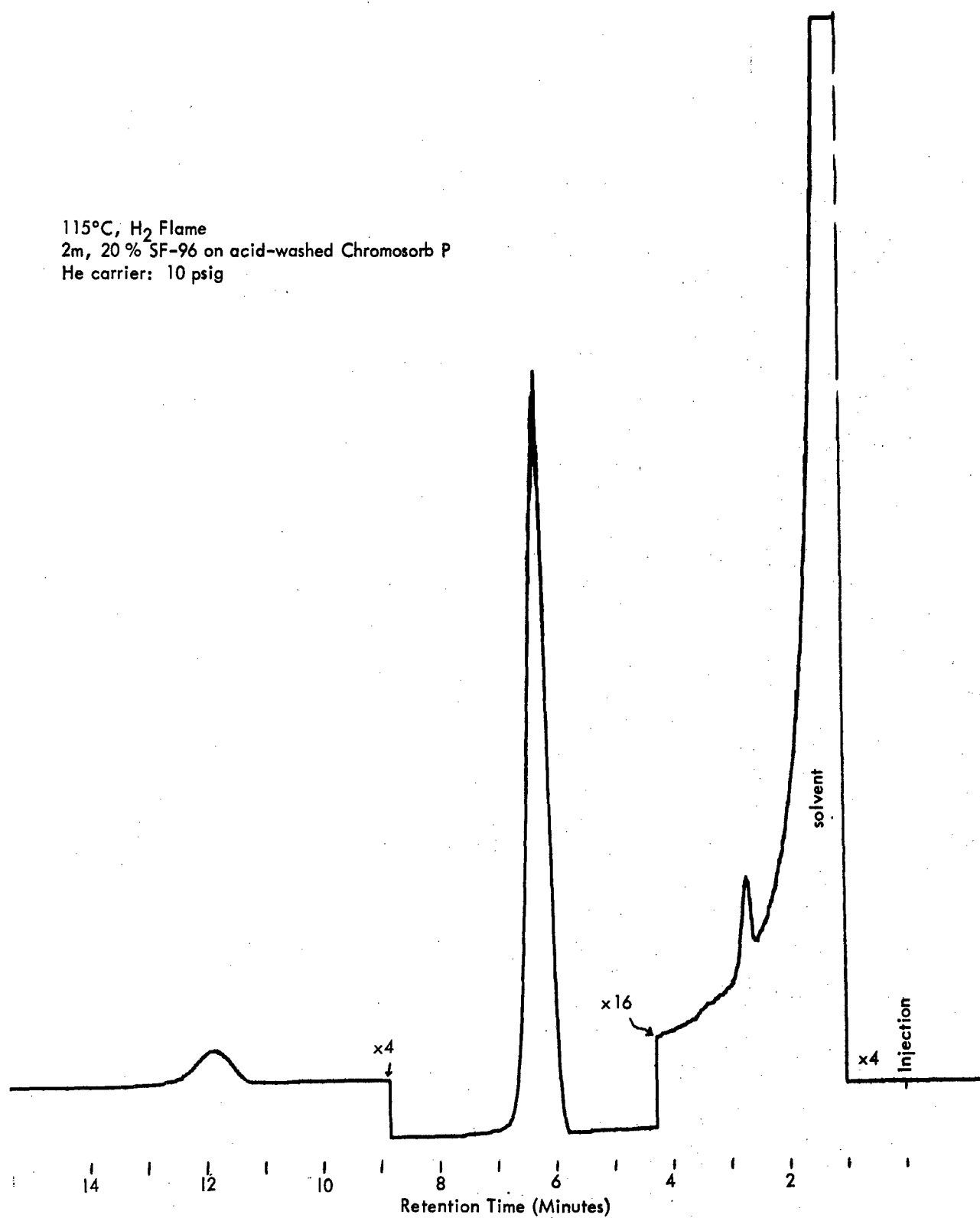


Figure 64 - Gas-Liquid Chromatogram of Lower-Boiling Fraction
(Perfluoro-n-decyl Iodide, 97.9% Pure)

115°C, H₂ Flame
2m, 20 % SF-96 on acid-washed Chromosorb P
He carrier: 10 psig

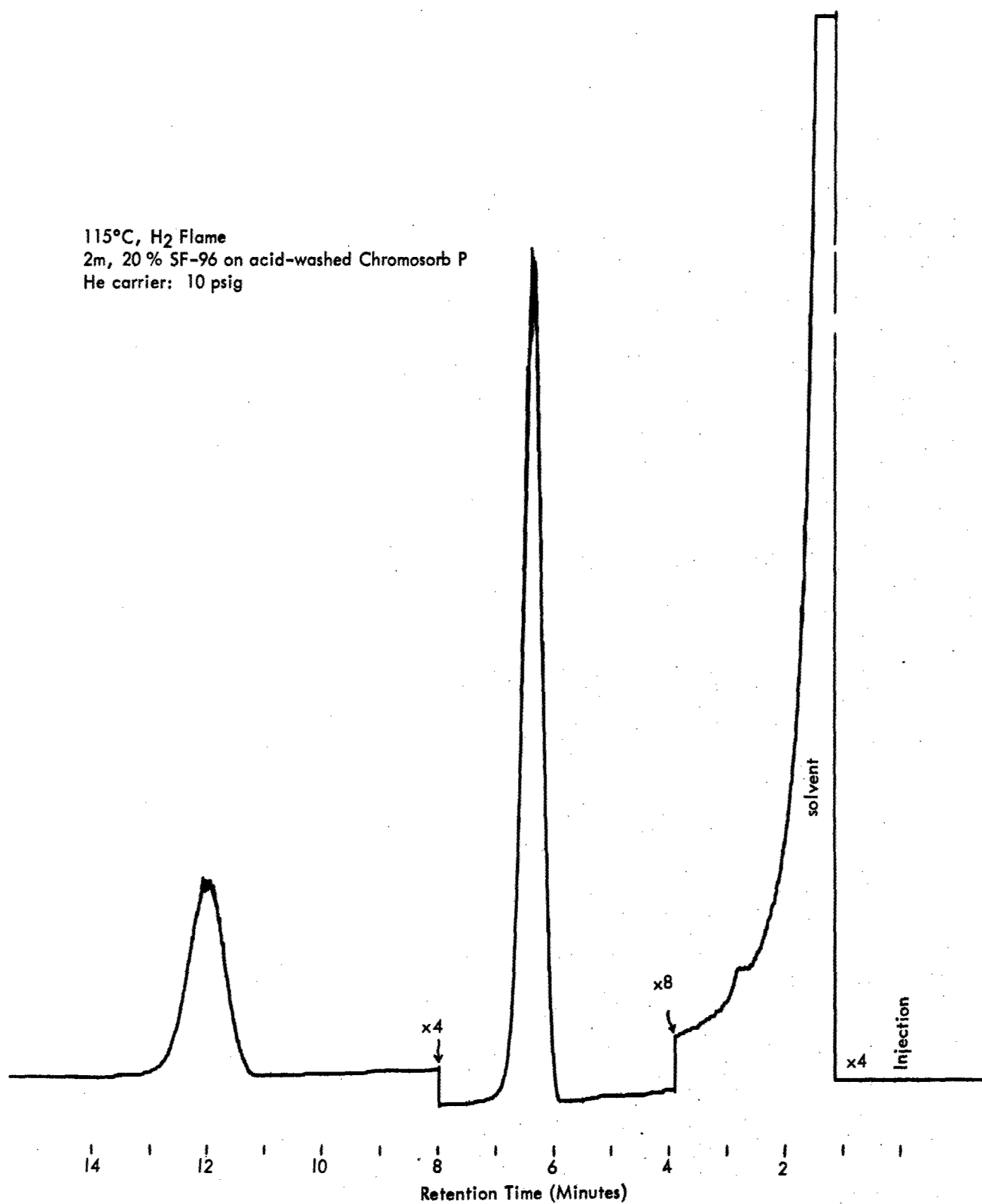


Figure 65 - Gas-Liquid Chromatogram of Distillation Residue
(Perfluoro-n-decyl Iodide, 82.8% Pure)

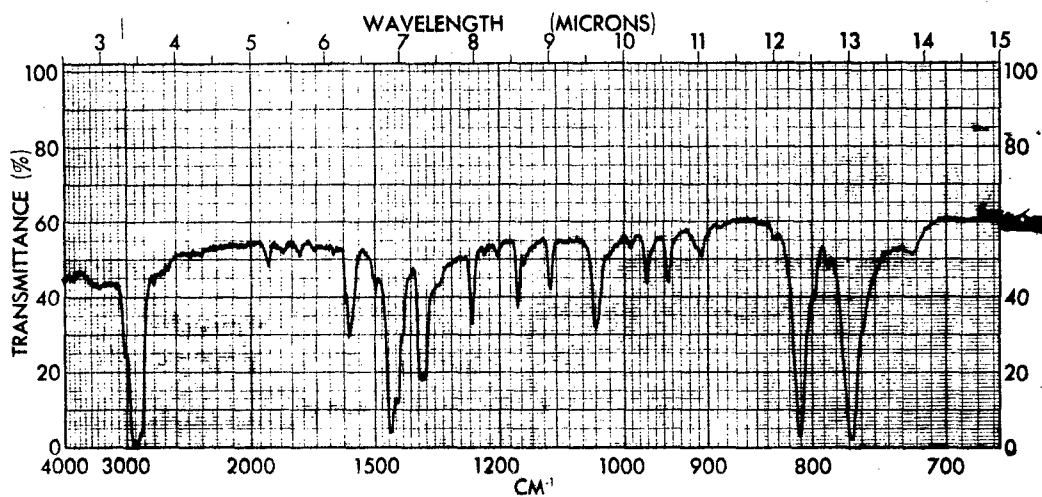


Figure 66 - Infrared Spectrum of Commercial Sample Reported
to be 1,8-Divinyl naphthalene (Nujol)
[Spectrum Corresponds to 1,8-Dimethylnaphthalene]

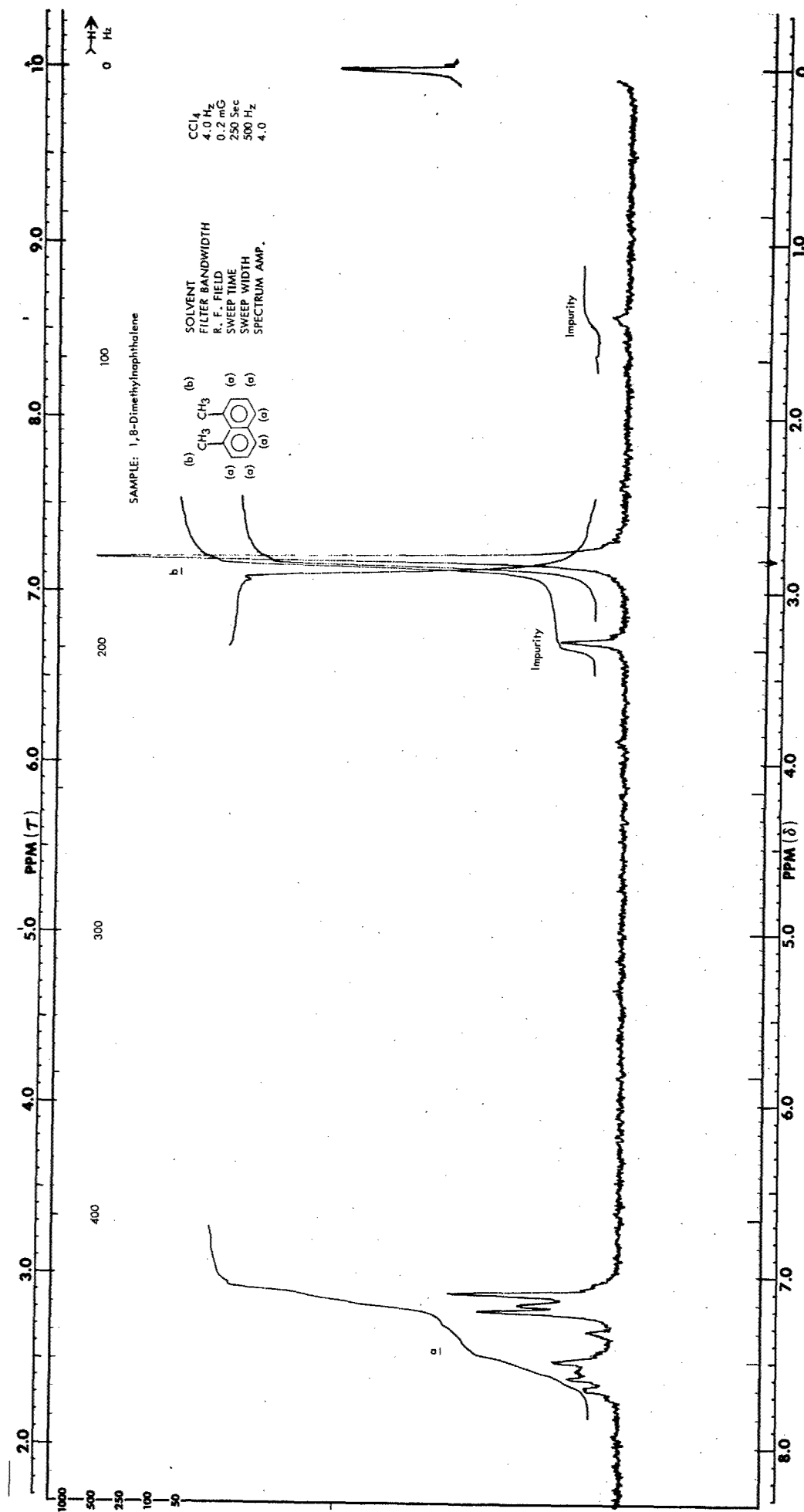


Figure 67 - NMR Spectrum of Commercial Sample Reported to be 1,8-Divinyl-naphthalene
 [Spectrum Corresponds to 1,8-Dimethylnaphthalene]

SAMPLE: 1,8-Divinyl-naphthalene

2 meter 5 % SF-96 on Gas Chrom Q

175°, He: 15 psig

Flame Ionization Detector

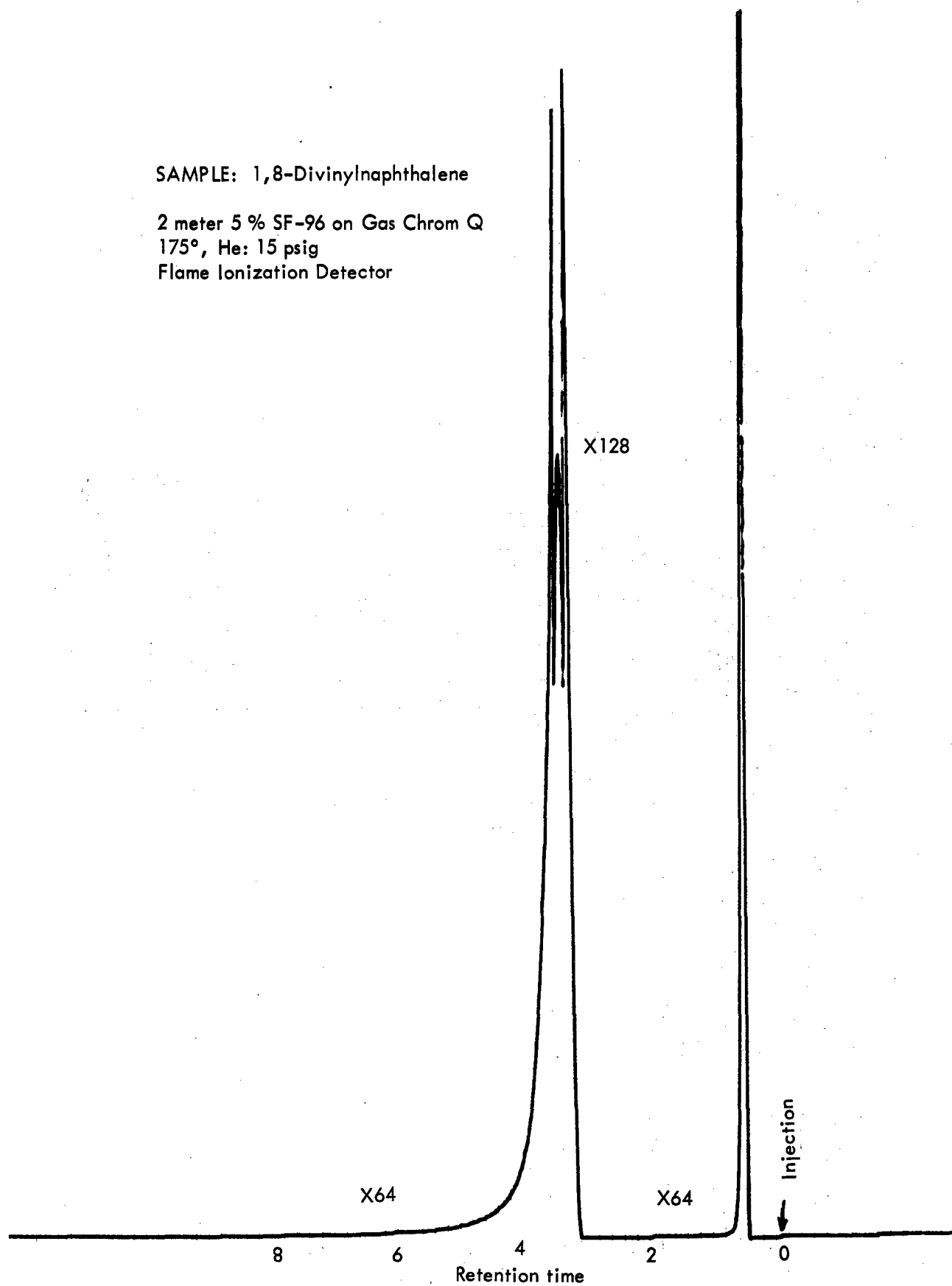


Figure 68 - Gas-Liquid Chromatogram of 1,8-Divinyl-naphthalene
(Sample 2)

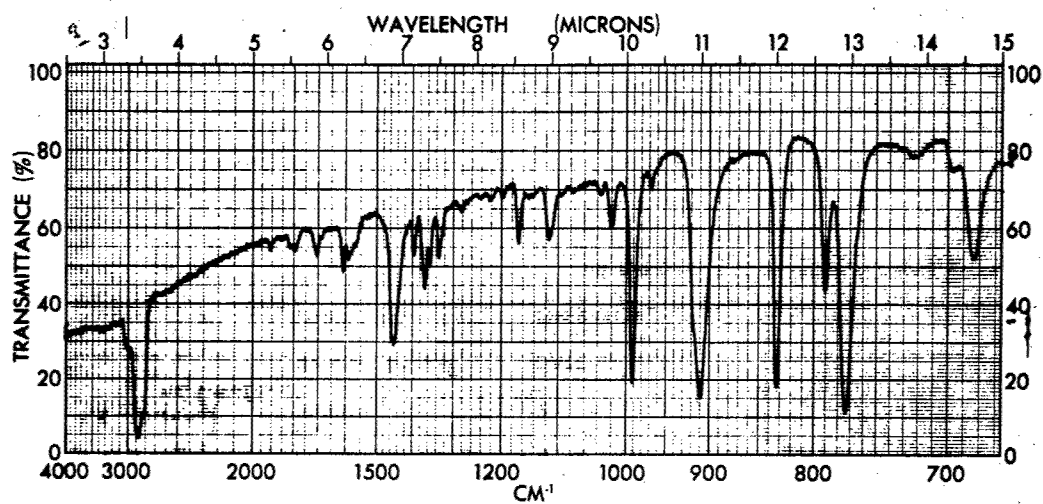


Figure 69 - Infrared Spectrum of 1,8-Divinyl-naphthalene (Sample 2)
(Nujol)

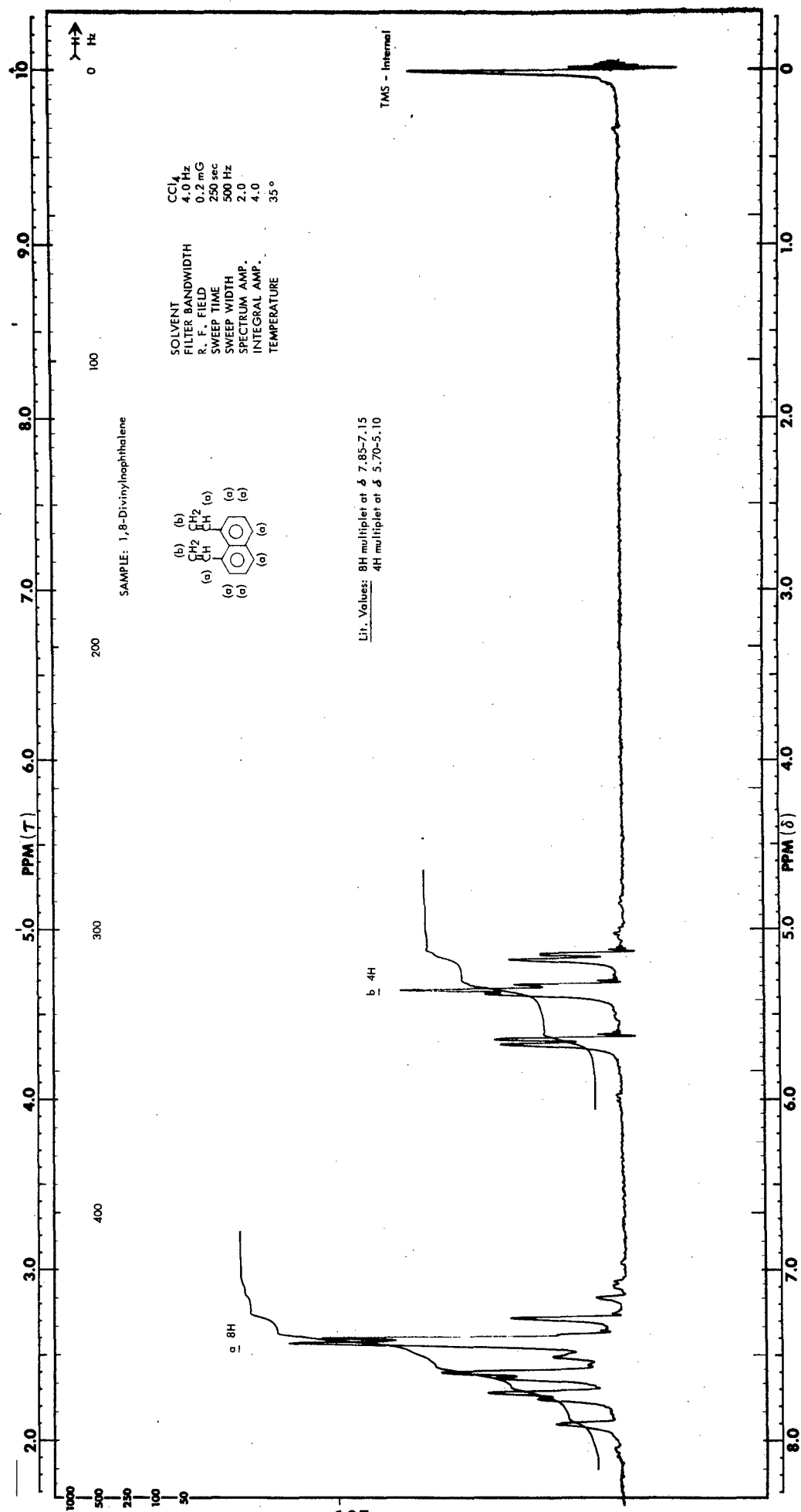


Figure 70 - NMR Spectrum of 1,8-Divinylnaphthalene (Sample 2)

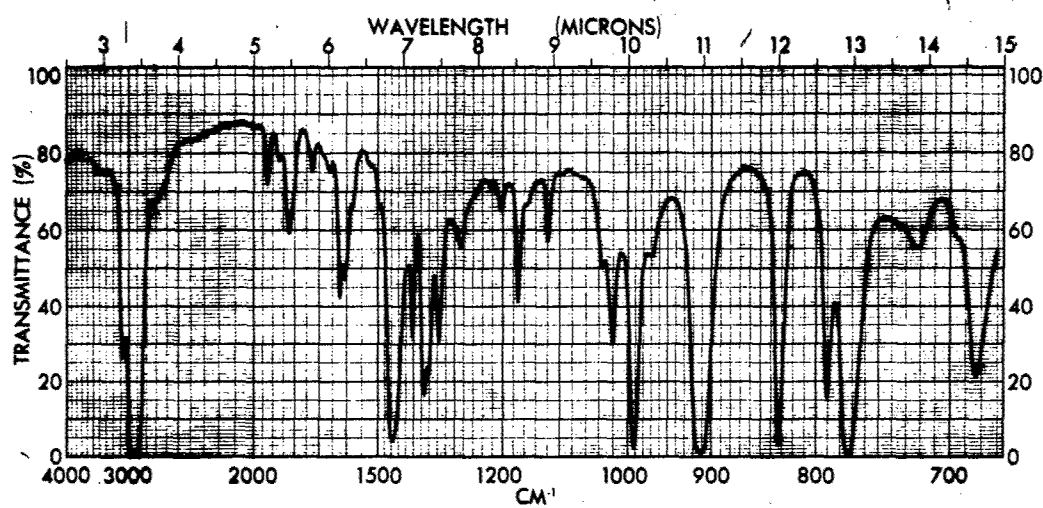


Figure 71 - Infrared Spectrum of 1,8-Divinyl-naphthalene (Sample 3)
(Nujol)

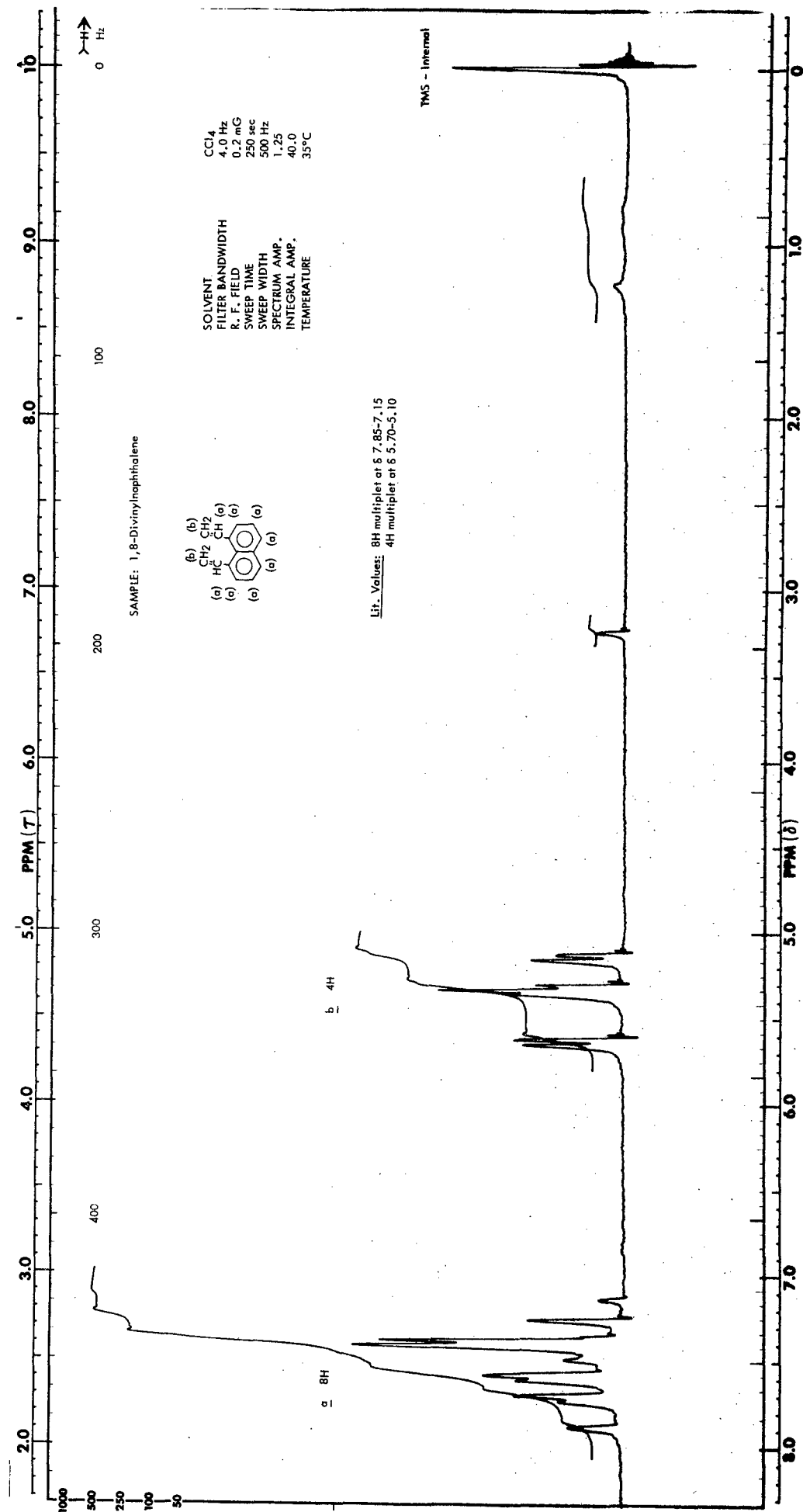


Figure 72 - NMR Spectrum of 1,8-Divinyl-naphthalene (Sample 3)

Sample: 1,8-Divinyl-naphthalene

2 meter 5% SF-96 on Gas Chrom Q

175°, He: 12 psig

Flame Ionization Detector

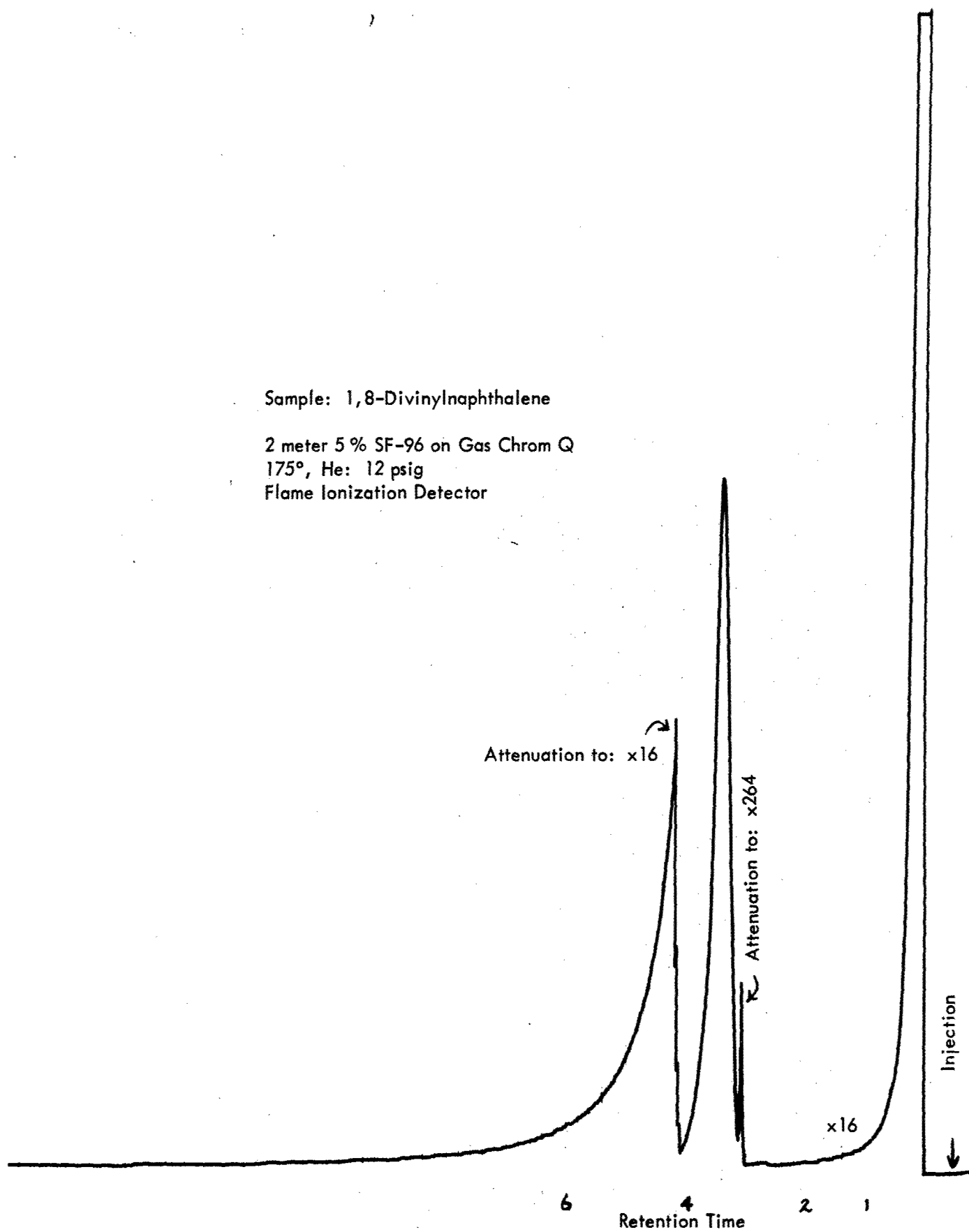


Figure 73 - Gas-Liquid Chromatogram of 1,8-Divinyl-naphthalene (Sample 3)

2,3,5,6-Tetrafluorothiophenol
2 meter 5% SF-96 on Gas Chrom Q 100/120 mesh
75°, He 15 psig
Thermal conductivity detector

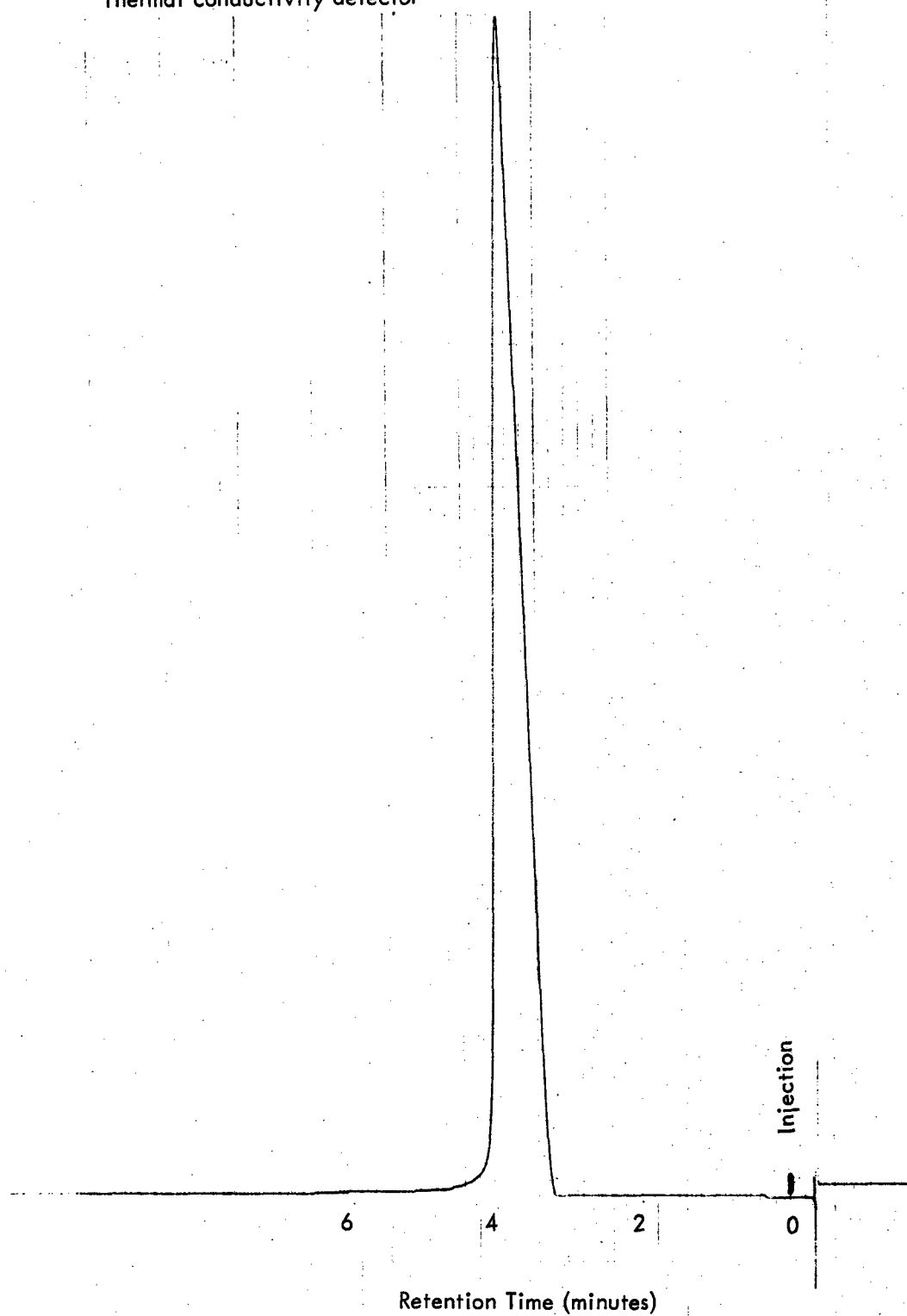


Figure 74 - Gas-Liquid Chromatogram of 2,3,5,6-Tetrafluorothiophenol

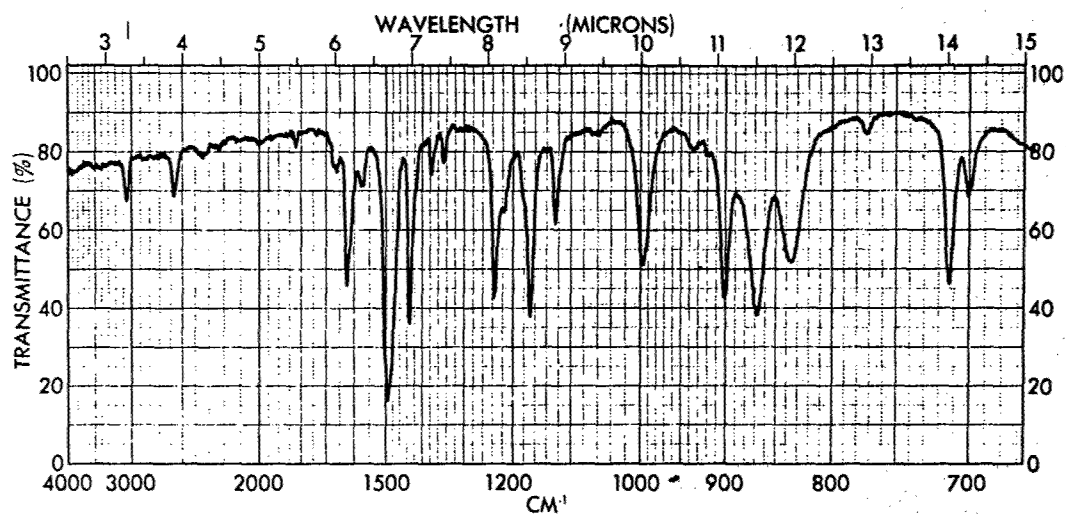


Figure 75 - Infrared Spectrum of 2,3,5,6-Tetrafluorothiophenol
(Liquid)

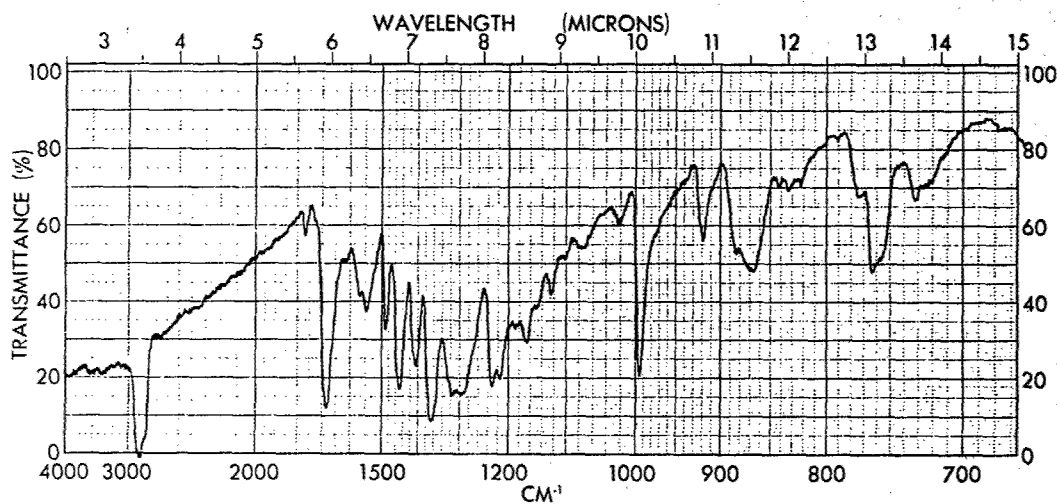


Figure 76 - Infrared Spectrum of BBL Polymer (Celanese 19273-34)
Unpurified (Nujol)

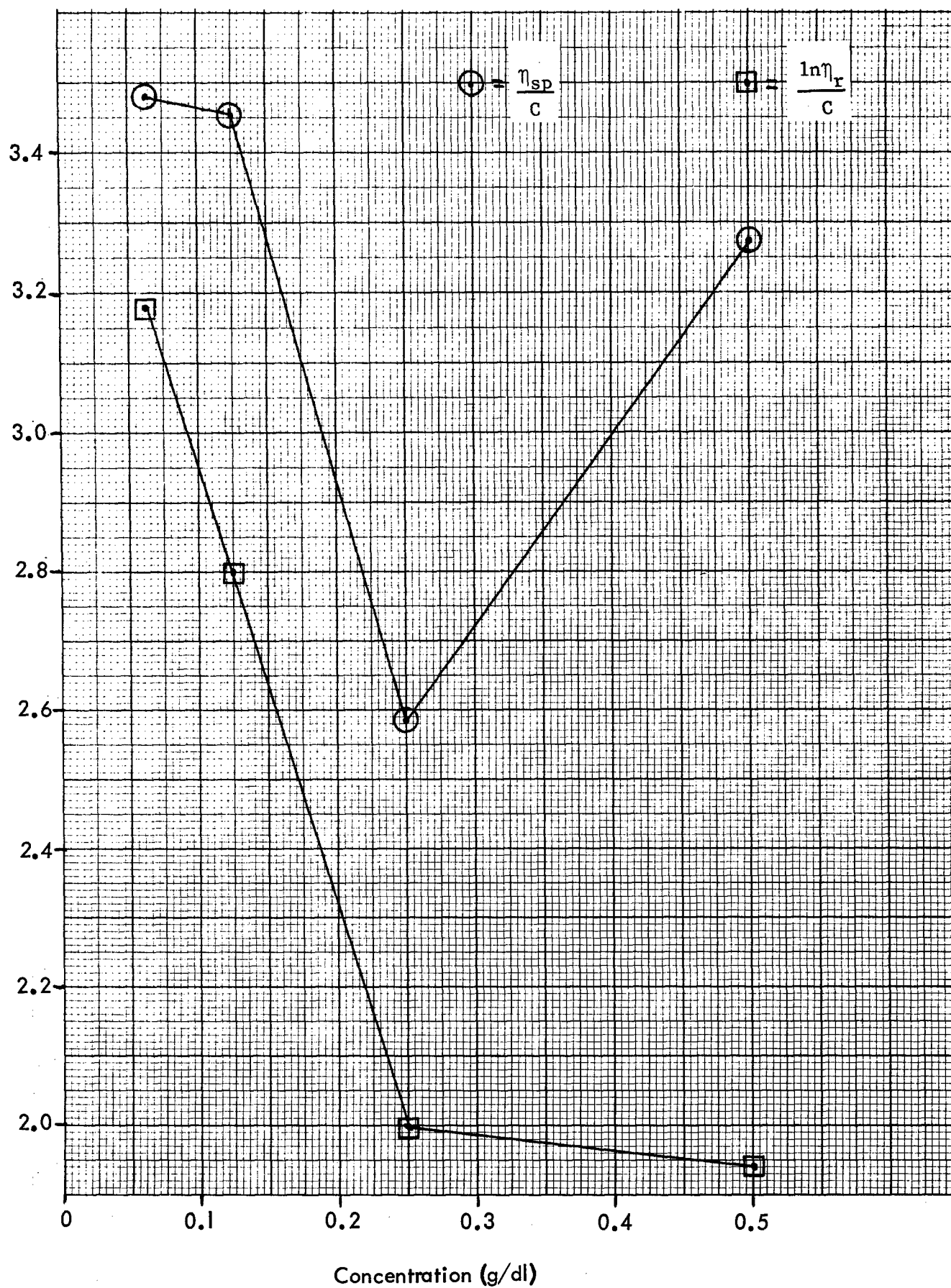


Figure 77 - Plot of Viscosimetric Data on BBL Polymer
(Celanese 19273-34) Unpurified

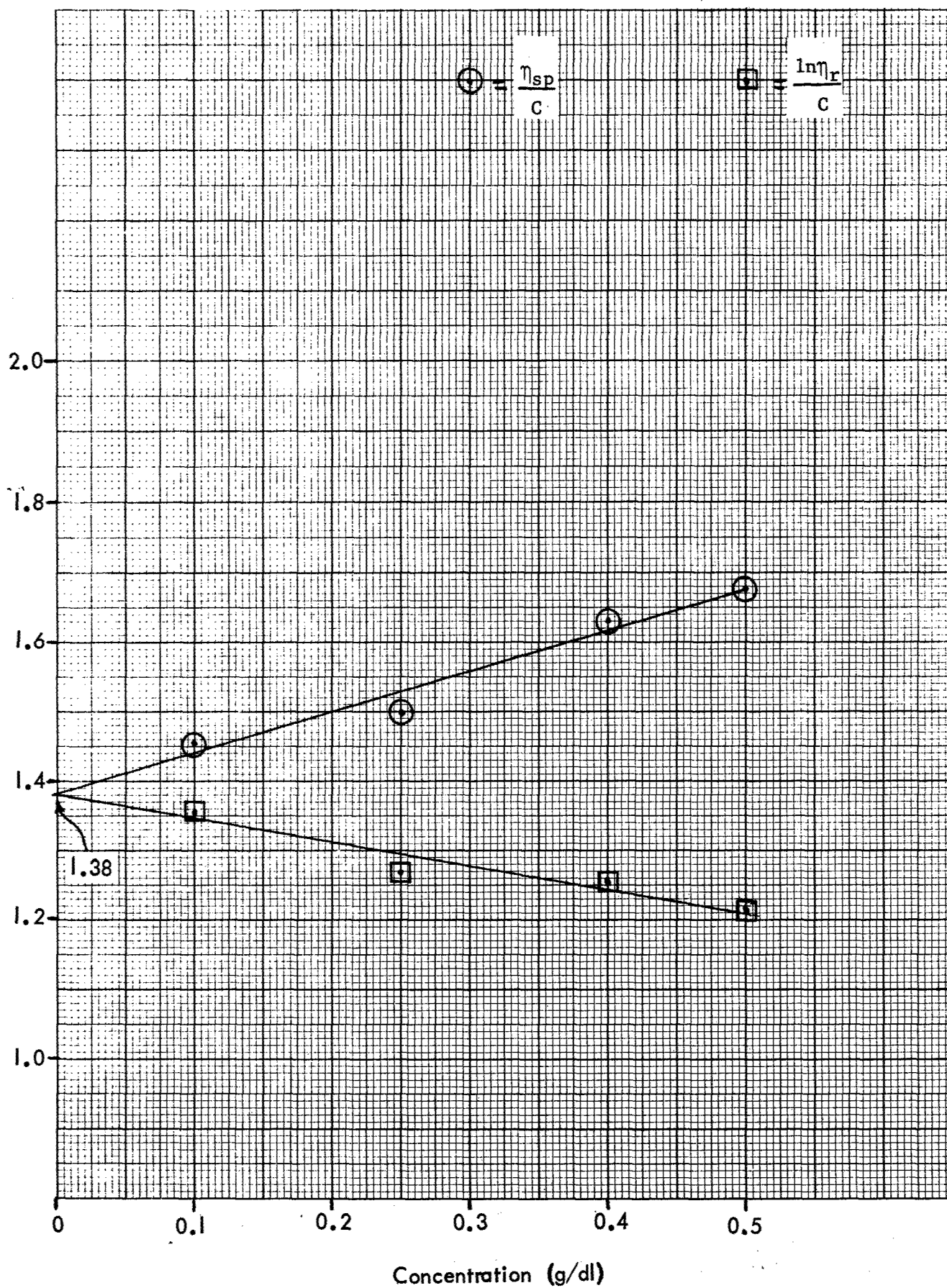


Figure 78 - Plot of Viscosimetric Data on BBL Polymer (Celanese 19273-34) Purified

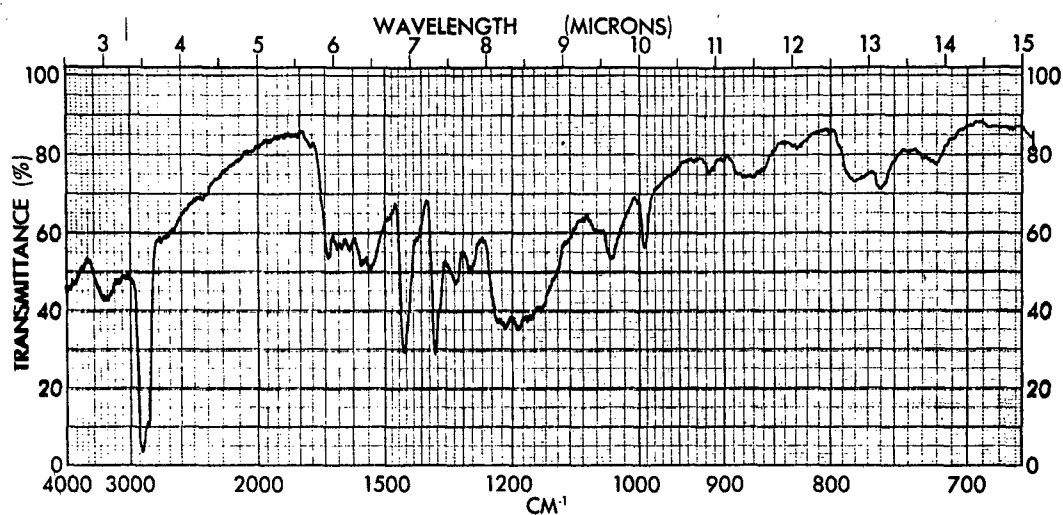


Figure 79 - Infrared Spectrum of BBL Polymer (Celanese 19273-34)
Purified (Nujol)

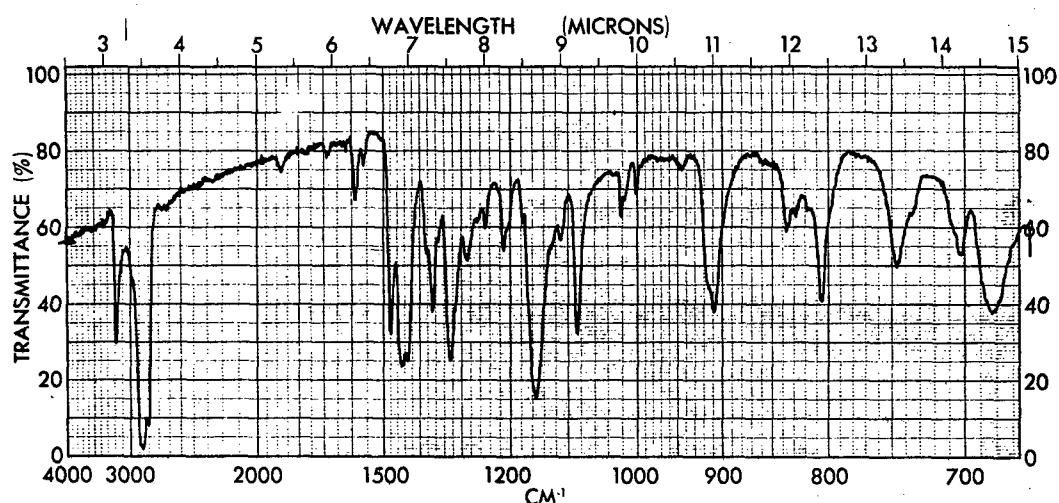


Figure 80 - Infrared Spectrum of N,N'-di-p-toluenesulfonyl Benzidine
(Nujol)

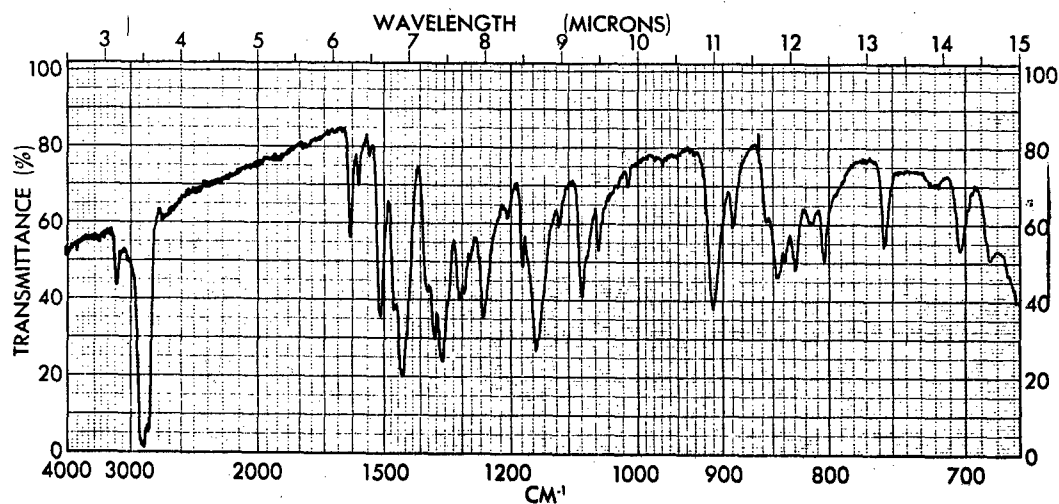


Figure 81 - Infrared Spectrum of 3,3'-Dinitro-N,N'-di-p-toluenesulfonyl Benzidine (Nujol)

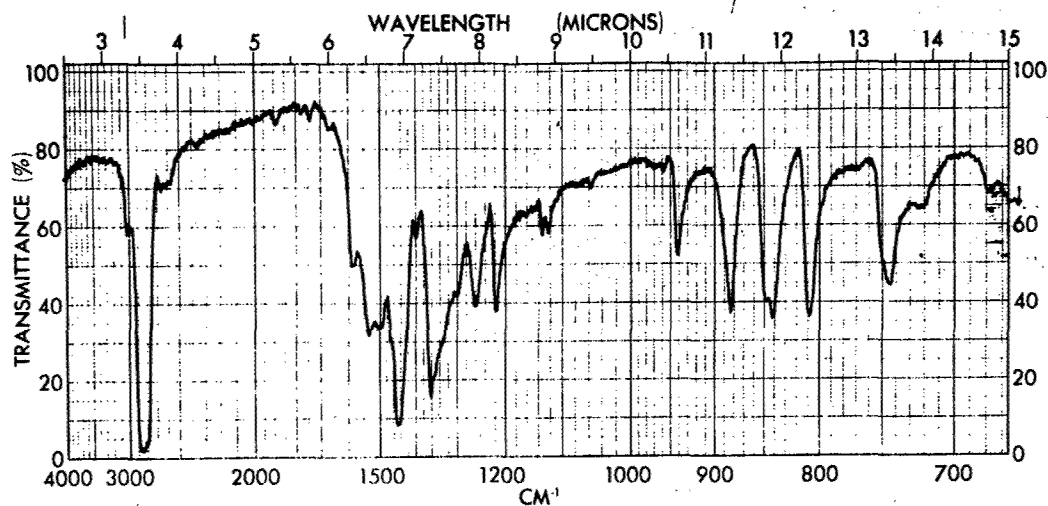


Figure 82 - Infrared Spectrum of 1,2-Dinitro-4-fluorobenzene (Nujol)

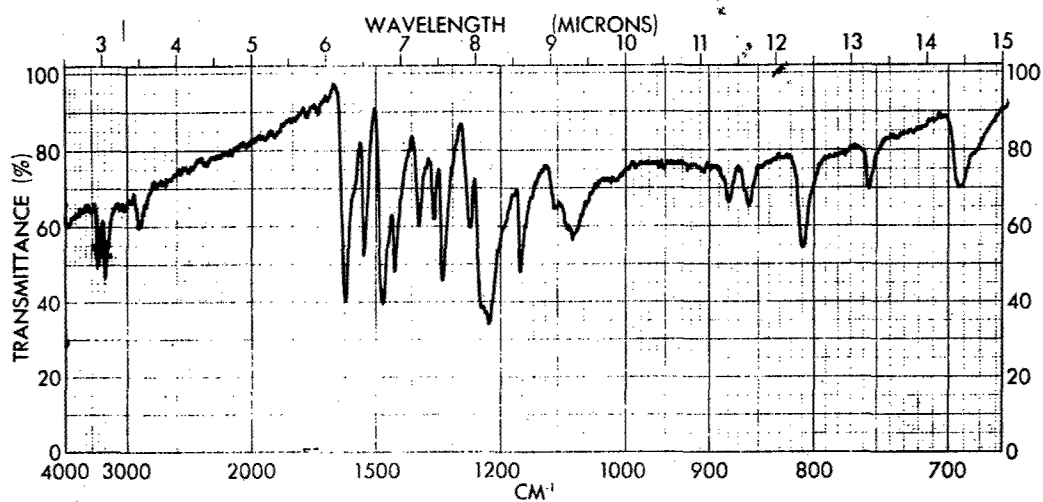


Figure 83 - Infrared Spectrum of p-Iodo-o-nitroaniline (KBr)

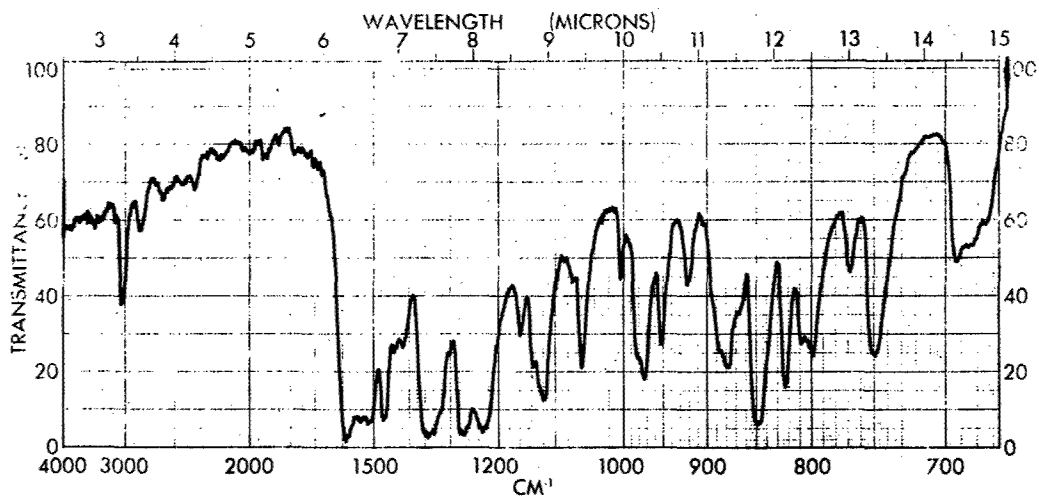


Figure 84 - Infrared Spectrum of 1,3-Bis(3,4-dinitrophenoxy)benzene (KBr)

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Security Classification

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13. ABSTRACT Work is reported on the synthesis and/or characterization of 30 different compounds for use in studies related to the preparation of high-temperature stable polymers. As a result of this effort, 28 synthesized and/or characterized compounds were submitted as 42 individual samples. The number and type of compounds submitted are identified as follows:															
<table border="0"> <tr> <td>2 - Perfluoro-n-alkyl iodides</td> <td>3 - Aromatic Disulfonamides</td> </tr> <tr> <td>2 - Divinyl substituted aromatics</td> <td>2 - Perfluoroalkylene bisphenols</td> </tr> <tr> <td>2 - Organo-diiodides</td> <td>2 - Perfluorophenyl thiols</td> </tr> <tr> <td>5 - Acenaphthene derivatives</td> <td>1 - Ladder polymer</td> </tr> <tr> <td>3 - Diether linked dicarboxylic acids</td> <td>3 - Substituted polyphenyl ethers</td> </tr> <tr> <td></td> <td>3 - Substituted phenyl halides</td> </tr> </table>				2 - Perfluoro-n-alkyl iodides	3 - Aromatic Disulfonamides	2 - Divinyl substituted aromatics	2 - Perfluoroalkylene bisphenols	2 - Organo-diiodides	2 - Perfluorophenyl thiols	5 - Acenaphthene derivatives	1 - Ladder polymer	3 - Diether linked dicarboxylic acids	3 - Substituted polyphenyl ethers		3 - Substituted phenyl halides
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	3 - Substituted phenyl halides														
<p>The 42 samples of the submitted compounds ranged in size from 2.0 to 650.4 g and, in nearly all cases, the purity was at least 99%. Mass spectrometry, infrared spectroscopy, gas liquid chromatography, nuclear magnetic resonance spectroscopy, thin-layer chromatography, differential thermal analysis, viscosimetry, and elemental analysis were employed to establish structure and determine purity.</p>															

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Monomeric Compounds						
Synthetic Methods						
Perfluoro- <u>n</u> -alkyl Iodides						
Divinyl Substituted Aromatics						
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